1955

Part I: Mechanisms of inhibited air oxidation of olefins. Part II: Reduction of nitro compounds with titanium III

Chester Eugene Hamilton
Iowa State College

NOTE TO USERS

PART I. MECHANISMS OF INHIBITED AIR OXIDATION OF OLEFINS

PART II. REDUCTION OF NITRO COMPOUNDS WITH TITANIUM III

by

Chester E. Hamilton

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1955

TABLE OF CONTENTS

PART I. MECHANISMS OF INHIBITED AIR OXIDATION OF OLEFINS

INTRODUCTION

The inhibition of air oxidation has been a problem extensively studied because of practical applications in preventing deterioration of many different materials between the time of manufacture and consumption of the various products.

Despite theories advanced by various workers in the field through the years and despite the great number of investigations carried forward (many of which had direct practical application) the manner in which a small amount of a certain material in the presence of another substance prevents attack on the latter by oxygen in the air had been and, in many cases, still is an uncertainty.

Since a knowledge of the mechanism by which inhibitors or antioxidants prevent air oxidation is of both theoretical and practical interest, this work was carried forward, with the purpose of obtaining some knowledge of the chemical reactions of inhibitors exposed to air in the presence of an easily oxidized material.

Since the products from the air oxidation of the inhibitor would, in conjunction with kinetic studies also being carried forward in these laboratories, give evidence of the mechanism by which inhibitors act, it was decided to attempt to isolate and identify these products.

In order to accomplish this purpose, a rather large amount of inhibitor in the presence of tetralin, a typical olefin whose air oxidation has been previously studied, or in an inert solvent, was air oxidized and work leading to separation and identification of products from the inhibitors was pursued.

HISTORICAL REVIEW

The first observation of an antioxidant effect followed by use of the antioxidant to prevent deterioration of a valuable product has been in all probability long since buried in antiquity. There has been a rather large number of reviews written[100,140,497,580,693,727,849,1024,1073] concerning various aspects of oxidation inhibitors. Le Bras[580] has attributed the first observation of an antioxidant effect to Boyle. Moureau and Dufraisse,[727] who published the first comprehensive review of the field, attributed the first observation of antioxidant action to Berthollet,[106] who observed that traces of sulfur vapor prevented the luminescence of phosphorus in dilute oxygen atmosphere. Other early observations were that of Deschamps[269] who observed that lard containing gum benzoin or populin did not become rancid as quickly as ordinary lard, and that of Chevreul[208] who observed that oak wood retards the drying of linseed oil.

In spite of these and other observations, the existence, much less the importance, of antioxidants, in both practical and theoretical aspects, was not widely recognized until Moureau and Dufraisse,[727] in 1922, began to publish observations on antioxygens.[100] Their entry into the field occurred October 21, 1917 during World War I, when in an effort to prevent acrolein polymerization, they added pyrogallol, another easily oxidizable substance, to the acrolein and found that oxygen absorption was inhibited and the acrolein did not polymerize. Following the war they continued to carry forward investigations of antioxidant substances and their properties. Recognizing that the formation of organic peroxides was associated with oxidative degradation, they postulated that antioxidants react with organic

peroxides, causing their decomposition while the antioxidant was regenerated. They also observed a close relationship between oxidation catalysis and inhibition and that in some cases this positive or negative catalysis depends on pH and substrate.

The practical success of Moureau and Dufraisse[727] in preventing polymerization of acrolein and their theories concerning antioxidants spurred the efforts of other workers to make both practical and theoretical contributions to this field. The rubber industry was vitally interested and was the first[140] to institute active research in the field. The petroleum industry, food processors, paint industry and others soon followed and the work has been increasing in an evergrowing flood to the present time.

One of the notable events of practical importance was in 1929 when Egloff and coworkers[305] published the first description of gasoline antioxidants, followed later by qualitative data concerning the effect of a large number of antioxidants on the length of the induction period before gum formation occurred in the gasoline.[306] In the years that followed, aromatic amines, phenolic and aminophenolic compounds were the only known effective gas antioxidants.[807] These were used along with copper deactivators such as the condensation product of salicylaldehyde and primary amino compounds. These compounds form complexes with traces of copper ion which often contaminate substances and the complex formation prevents deleterious effects which would occur should the copper be allowed to catalyze air oxidation of the gasoline.

Workers in vegetable and animal fats and oils were also concerned with antioxidants. Theirs was a two-fold interest since they recognized the

existence of naturally occurring oxidation inhibitors which they desired to identify and evaluate and they were also interested in more effective antioxidants. After Olcott and Emerson's[777] work with naturally occurring vitamin E and the establishment of its structure by Ferholz,[324] Golumbic[386] in 1943 was able to show that vegetable oils contained tocopherol (vitamin E) which oxidized rapidly to tocoquinone and then more slowly to chroman-5,6-quinone. It was shown later that γ-tocopherol gives the same quinone.[1024] It was during the slower oxidation that organoleptic rancidity occurred and before peroxide concentration increased rapidly. Thus the difference in stability of vegetable and animal fats was explained since animal fats contain very little vitamin E. Since there is an optimum concentration of tocopherol for maximum inhibition[387,779] the fact that addition of tocopherol to vegetable oil had no beneficial effect, whereas the opposite is true with animal fats, is thus explained.

In addition to vitamins C and E, other naturally occurring substances or their derivatives have been fruitful sources of highly efficient antioxidants. Gossypol was obtained from cottonseed and described by Mattill[651] in 1931. In 1941 Sabalitschka and Boehm[898] first patented the alkyl esters of gallic acid as antioxidants and Boehm and Williams[128] described the properties of propyl gallate in 1943. Nordihydroguaiaretic acid obtained from creosote bush was described by Lundberg, et al. in 1944.[626] Those most recently reported were norconidendrene[338] from western hemlock trees reported in 1947 and aca-catechin[486] from a bush native to India reported in 1951.

Although the results of the investigations to find efficient antioxidants and of the determination of how and where to use them have been

quite successful, the theories so far advanced to explain antioxidant action have not been able to explain all the facts or forecast with any certainty the results to be expected from a given antioxidant in a given system. However these theories have proved of value in being a guide to further study. The theory of Moureau and Dufraisse[727] that the organic peroxides formed by autoxidation of the substrate are decomposed by the antioxidants with a regeneration of the antioxidant soon came into question because it began to be recognized that the antioxidant was oxidized during the inhibition period. Also, if there was regeneration of the antioxidant, the inhibition period should be infinitely long, which was not the case. In 1929, Alyea and Backstrom[22] concluded from their kinetic studies that autoxidation was a chain reaction and that antioxidants interrupted the oxidation chain and were themselves oxidized in the process. They were noncommittal about the actual mechanism, referring to energy chains, but not specifying how the energy was transmitted. A modification of the Moureau and Dufraisse theory[727] had also been suggested. Since it had been recognized from the beginning that an inhibitor must be an easily oxidized substance and it was now recognized that the inhibitor was oxidized during the inhibition period, it was suggested that the inhibitor reduced the organic peroxides formed.[262,681] Largely on the basis of kinetic evidence[22,73,1161] this idea is not now widely accepted, although kinetic evidence has recently been imputed by Shelton and co-workers[933,934] to imply that amines (and carbon black) do not break oxidation chains, but destroy peroxide and are probably different than phenols in rubber. However, Kuzminskii[568] showed that 2-naphthylphenylamine does not destroy rubber peroxide at 80° under a nitrogen atmosphere. He reports, on the

other hand, that di-p-hydroxyphenylamine, p-hydroxyphenyl-2-naphthylamine and trihydroxybenzene react with stable rubber peroxides. He feels this effect may occur but is not the primary cause of inhibition. He states that a good inhibitor should be a substance that gives up mobile hydrogen to peroxide radicals, thus breaking the chain and that it is necessary that the product from the inhibitor must be stable and must not be a chain transfer agent. Also as recently as 1948, Michaelis[685] suggested a sort of cyclic mechanism where peroxide oxidizes hydroquinone to semiquinone and then reverses the process in some cyclic mechanism so that the peroxide is so short-lived in this cycle that it has no chance to break down and induce the slower irreversible reactions which result in the oxidation of the fatty acid substrate. This would seem to be substantially a reproposal of the old theory of Moureau and Dufraisse.[727]

Other material of theoretical interest has been the evaluation of oxidation-reduction potentials of quinhydrone-type compounds and the critical oxidation potentials of other antioxidants which do not go to an oxidation product by an easily reversible process. After data of this type was obtained, an attempt was made to correlate the data with the efficiency of antioxidant action of various compounds.[133,326,620,693] The potentials of the best inhibitors were between 0.6 and 0.8 volts, although some compounds in this range were not good inhibitors. This being the case, oxidation-reduction potentials could not be relied on to evaluate a substance as an inhibitor, although theoretically this should have been the case since the ease with which an electron can be removed should be related to the ease with which the antioxidant can be oxidized. The fact that quinols, which are usually good inhibitors, form a semiquinone reversibly on oxidation

led to the suggestion that phenolic oxidation proceeds in two steps,[222,326,686] the first a reversible step and the second not usually so.[222]

The effect of structure has been of importance in attempts to explain antioxidant activity. In 1934, Olcott[775] showed that polyhydroxybenzenes were good antioxidants, but that hexahydroxybenzene exhibited no antioxidant action in spite of being easily oxidized. This is illustrative that mere ease of hydrogen removal is no guarantee of an effective antioxidant.

However, because many good inhibitors do have labile hydrogens, there still exists an impression that ease of hydrogen removal is a necessity in a good inhibitor in order that peroxy radicals may abstract the hydrogen, thus breaking the chain, provided the product from the inhibitor is stable.[568] The studies of Murphy, et al.[734] with phenothiazine derivatives is another case in point. They found that the first oxidation product of phenothiazine was phenothiazine-5-oxide which is almost as efficient an inhibitor as the first compound. This will form phenothiazine-5-dioxide on further oxidation and is no longer a good antioxidant, although there is still hydrogen available on the nitrogen atom. Substitution of alkyl radicals for the hydrogen impair the antioxidant properties of the original compound although the N-octadecyl and N-benzyl derivatives are nearly as efficient.

Other authors have studied the effect of varying substituents on various phenols and aromatic amines on antioxidant efficiency, as well as structure of hydrocarbons acting as antioxidants.[112,133,568,620,882,883,953] Substituents releasing electrons to the aromatic ring enhance antioxidant activity.

Recently Campbell and Coppinger[181] reported that 2,6-di-t-butyl-p-cresol formed 1-methyl-1-t-butoxy-3,5-di-t-butylcyclohexadienone-4 when di-t-butylperoxide was decomposed in its presence and proposed that two $RO_2\cdot$ with the same phenol should give the same type compound. Cook[223] objected to this as a general mechanism of antioxidant action on the basis that he had obtained a dimerization product, 3,3',5,5'-tetra-t-butyl-4,4'-dihydroxydiphenylethane, on oxidation of the phenol with PbO_2 or H_2O_2. He mentions that this product was still a fairly efficient antioxidant. He cites other like products isolated by other workers in an attempt to show the generality of dimer formation. Moore and Waters[704] also report isolating the same product in small yield from a free radical oxidation reaction. However, Bickel and Koojman[110b] isolated the suggested peroxide derived from the phenol and $(CH_3)_2C(CN)O_2\cdot$ in 1953. This would mean that two peroxy radicals react with the phenol as compared to the one which would be necessary from Cook's dimerization product, if the dimer oxidized no further. In the case of Cook's product, it does go to 3,3',5,5'-tetra-t-butylstilbene-4,4'-quinone, which would require that three radicals react with each phenol molecule. Kinetic evidence on stoichiometry is in order.

Two authors other than Boozer and Hammond[135] have suggested complex formation is related to antioxidant effect. Jacquemain and Berger[496] postulated that "positive catalysis" occurs at low (inhibitor) concentration because the inhibitor is associated with reacting substance, while at high concentration the association occurs mostly between molecules of inhibitor, thus explaining the antioxidant property of phenol at high concentration and its oxidizing properties at low concentration. Chamberlain and Walsh[193,1114] postulate that there is a complex formed in the gas phase

between the inhibitor and the radical chain carriers since they observed a correlation between antiknock effect and the influence of side chains on the electronic properties of aromatic rings. Those substituents which released electrons to the rings promoted antiknock effect.

Another problem of theoretical and also practical interest is that of synergism. Lea[575] states that true inhibitors are usually oxidized while synergists enhance the activity of phenolic antioxidants. Many substances are synergists of another substance and no general theory has yet been applied. However, ascorbic acid is widely used and Calkins and Mattill[180] proposed that the antioxidant quinone was reduced by the synergist and the semiquinone then oxidized to quinone by the activated peroxide which was reduced in the process. Golumbic[387] found that benzoquinone and α-tocoquinone were good antioxidants if phosphoric acid were present and stated these compounds were reduced to the hydroquinone form by the fat substrate since a biological assay showed vitamin E activity upon addition to a fat of α-tocoquinone and phosphoric acid. Le Bras[579] found that phenyl-2-naphthylamine and mercaptobenzoimidazole were synergists. He proposed that the amine stopped reaction chains, since it decreased oxygen absorption and that the other compound, which had slight effect on the oxygen absorption rate, deactivated the peroxides formed.

In protecting material from oxidation not only are antioxidants and synergists used but also substances which form inactive complexes with prooxidant metals. This is particularly true in lubricants. Very complex substances are used which not only perform one or all antioxidant functions but also impart other desirable properties as well. Such substances are various sulfides,[262] complex thiophosphoric acids,[68] and others. Such a

vast amount of work has been done in the field in the last ten years alone that it is staggering. These and other substances have been listed in the following table. An effort has been made to make as complete a literature survey as possible of the work done in the last ten years. Much of the material was read only as found in Chemical Abstracts. No doubt there are omissions and errors since there are so many references. A few patents were not included since they could not be relocated by patent number in Chemical Abstracts. Others were not included which seemed to be very similar to other patents previously noted. The abstracts were searched page by page from January through September 1954. No doubt pertinent information has been overlooked. It is hoped that the compilation might prove serviceable. Where no designation is made in the table concerning the use of the antioxidant, none was indicated in the abstract.

From the previous discussion of theoretical investigations, it will be observed that little is known of the reaction products obtained from the air oxidation of antioxidants in a simple substrate. Most investigations have ignored this possibility of gaining an insight into the mechanism of inhibitor action. It is for this reason that the following work has been carried forward.

Table 1

Antioxidant literature survey

Type	Antioxidant for R[b]	G[c]	C[d]	L[e]	P[f]	E[g]	F[h]	S[i]	M[j]	A[a]	Ref.
Aromatic hydroxy compounds											
A. Catechol derivatives											
Monobenzylcatechol	X										941
p-t-Butylcatechol	X			X					X	Amines or inorganic hydroxides - 349	336, 454 870, 941

[a]Accompanying substances or synergists and their references.

[b]Elastomers.

[c]Gasoline and fuels.

[d]Carotene and vitamins.

[e]Lubricating and mineral oils.

[f]Paint oils.

[g]Edible oils and fats and derivatives.

[h]Foods and flavors.

[i]Soaps and waxes.

[j]Miscellaneous.

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Catechol		X	X	X	X	X	X		X		51, 54, 112, 128, 130, 454, 501, 528, 577, 591, 592, 624, 730, 744, 746, 909, 781, 983, 1029, 1036, 1110
Acetone-pyrocatechol cond. prod.		X									592
Hexylcatechol		X		X				X	X	P_2S_5 isobutylene reac. prod. - 869	
Stannous salt of o- or p-phenylcatechol	X										8
Stannous catecholate	X										957, 959
Phenylethelcatechols (1,2-dihydroxy-4-(1-phenylethyl) benzene								X			183
Aca-catechin											486
Extract of Larrea Divaricata bush						X					814

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Nordihydroguaiaretic acid (NDGA)			X			X	X	X	X	Amino acid - 623 Ascorbic acid - 626, 1135 Ascorbic or citric acid - 169 Ascorbic, citric or phosphoric acid - 358 Ascorbic acid in Irish Moss extract - 1011 Ascorbyl palmitate - 380, 1159 Citric acid and tartaric acid - 260, 274, 873 Ethylvanillate or benzoic acid - 944 Methionine, ascorbic or citric acid - 1018 Methionine, phenylalamine, milk protein hydrolysate #1 - 214 $Na_2S_2O_5$ - 1133 $(NaPO_3)_6$ and Mandrell's salt - 586 Oat flour - 872 Phospholipid or citric acid - 116	56, 123 151, 158 161, 194 195, 215 239, 245 248, 342 351, 357 360, 378 379, 393 439, 445 520, 524 526, 537 538, 551 556, 562 570, 583 603, 624 648, 649 690, 695 703, 709 710, 722 728, 735 740, 741 756, 828 858, 896 905, 956 982, 983 1017, 1018 1019, 1020 1021, 1025 1026, 1028 1029, 1069

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
										Thiodipropionic acid - 816	1079, 1087 1163
Adrenaline						X					744, 951
Quercitin						X					438, 567 854
Quercitrin						X					854
Rutin						X					854
Chalcone of hesperidin						X					854
Hematoxylin						X	X				55, 577 616
Gossypol						X	X		X		44, 111 468, 469 956
Dianilinogossypol						X			X		111, 468 469
Norconidendrin						X					337, 338 703
3,3,3',3'-Tetramethyl-6,6',7,7'-tetrahydroxy-1,1'-spirobisindane									X		167
Sesamol						X					160, 703

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Ethylhydrocaffeate							X				1020
Dihydroquercetin (pentahydroxyflavinone)						X				Citric acid - 567	
Ethylprotocatechuate						X					357
Esters of protocatechuic acid						X					785
Piperonal ⟶ $3,4(HO)_2\text{-}C_6H_3CHO$ ⟶ caffeic acid						X	X				738, 1027
3,4-Dimethylesculatin						X					1027
3-Isopropyl-4-methylesculatin						X					1027
3,4-Dimethyldaphnetin						X					1027
4-Methyl-3,4-dihydroesculatin						X					1027
4-Methylesculatin						X					1027
Esculatin						X					1027
Daphnetin						X					1027
4-Methyldaphnetin						X					1027

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Protocatechuic acid ($(HO)_2 \cdot C_6H_3 \cdot COOH + H_2O$)			X	X		X					591, 760 577
α,ω-Bis(hydroxyphenyl) alkanes (1,4-bis(3,4-dihydroxy-phenyl) butane) (1,5-bis(3,4-dihydroxy-phenyl) pentane) (1,6-bis(3,4-dihydroxy-phenyl) hexane)		X		X							381, 1000
Divanillal acetone							X		X		500
Divanillyl acetone							X		X		500
Divanillylisopropanol							X		X		500
Divanillalisopropanol							X		X		500
Diisoeugenol							X				499
Isoeugenol and syringic acid							X				499
Safrole											410
Isoeugenol											410
Cis-isofroeugenol											410

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Guaicol						X					983
Carbonyldihydroxy derivative of diisosafrole						X					936
Isosafroeugenol						X					357
Cond. prod. of phenol and eugenol						X					937
Cond. prod. of eugenol and HCHO						X					937
∝-Conidendrol	X					X					634
β-Conidendrol	X					X					634
Vanillas							X				829
Eugenol (1,4,3) $[C_3H_5 \cdot C_6H_3(OH)(OCH_3)]$								X			410, 1081
Dihydrocaffeic acid						X					307, 1027
Hydrocaffeic esters						X					307
Methyl caffeate						X					1027
Ethyl caffeate						X					1027
Propyl caffeate						X					1027

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Methyl dihydrocaffeate						X					1027
Ethyl dihydrocaffeate						X					1027
Propyl dihydrocaffeate						X					1027
Ethyl protocatechuate						X					1027
B. Pyrogallol derivatives											
Pyrogallol	X	X	X	X	X	X	X		X	Maleic anhydride - 593 $Na_2S_2O_5$ - 1133, 1134	100, 130 131, 138 112, 182 280, 351 501, 526 539, 577 614, 648 683, 730 744, 781 805, 909 912, 983 1029, 1092 1027, 1097 1110
Pyrogallol-acetone cond. prod.						X					577
Caprylpyrogallol		X		X				X	X	P_2S_5 isobutylene reac. prod. - 869	
Gallacetonin							X				648

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Dihydropyrogallol							X		X		1160
Pyrogallol derivatives			X								113
C. Resorcinol derivatives											
Mono-t-butylresorcinol	X										940
Di-t-butylresorcinol	X										940
Di-sec-amylresorcinol	X										940
Resorcinol	X		X		X	X	X		X	Furfural - 487	133, 501, 527, 528, 781, 909, 1027, 1036, 1110
5-Pentadecylresorcinol						X	X				59
Acyl derivatives of resorcinol			X								527
Alkylated resorcinol (2,4,6-triethyl resorcinol)			X								527
D. Gallic acid derivatives											
2-[o-(o-Triacetyl) gallyl] phloroglucinolaldehyde						X					745

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Propylgallate			X			X	X	X	X	Ascorbic acid - 1031 Ascorbyl palmitate - 657 Ascorbyl stearate - 710 β-Aminoethanol bound to glycerol-phosphoric radical - 553 Butylated hydroxy-anisole - 546 Citric acid - 393 Citric or phosphoric acid - 551, 562 Citric or tartaric acid - 138 Lecithin - 1094 $(NaPO_3)_6$ and Mandrell's salt - 586 Oleic acid - 76	74, 75 78, 129 130, 158 161, 210 220, 278 293, 357 414, 431 445, 517 520, 537 560, 583 584, 603 637, 702 703, 722 729, 735 756, 784 872, 900 904, 905 983, 896 1021, 1022 1028, 1020 1029, 1032 1069, 1163
Butylgallate			X			X	X		X	Citric acid - 137, 574 Citric or phosphoric acid - 562	55, 130 616, 1032
Methylgallate						X					158, 896
Amylgallate						X					158

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Ethylgallate			X			X	X	X	X	Ascorbic acid - 1031 Citric acid - 393 Citric or phosphoric acid - 562 Citric or tartaric acid - 138	42, 55, 158, 161, 330, 351, 576, 577, 578, 616, 786, 896, 1020, 1021, 1027, 1032, 1033, 1070, 1163
(5,6,7,5',6',7'-Hexahydroxy-3,3,3',3'-tetramethylbis-1,1'-spirohydrindene) gallic acid						X					577
Esters of above						X					577
Gallic acid						X	X				158, 328, 624, 722, 744, 745, 828, 896, 897, 955, 983, 1011
Hexylgallate						X	X				158, 1032
Decylgallate						X	X				158, 1072
Laurylgallate						X	X			Citric acid - 638	983

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Octylgallate						X	X			Citric acid - 393	158, 562, 722, 849, 1065, 1069, 1070, 1072
Cetylgallate						X	X				41, 158, 562, 1072, 1096
Dodecylgallate			X			X	X	X	X	Citric acid - 393 ($NaPO_3$) and Mandrell's salt - 586	41, 158, 345, 562, 722, 849, 1021, 1065, 1069, 1072, 1096, 1159, 1163
Tetradecylgallate						X	X				722, 1065
Hexadecylgallate						X					562, 722
Octadecylgallate						X					722
Digallic acid							X				243
Glycerol monogallate dipalmitate							X				119
Glycerol monogallate monostearate							X				119
Morpholonium gallate			X			X					552

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Low molecular weight gallic acid esters			X			X	X			Benzoic, fumaric, tartaric, citric, phosphoric and ascorbic acids - 416 Lecithin and tocopherols - 413	107, 112, 414, 1067
Trishydroxymethyl-methylammonium gallate			X			X					552
Gallic acid salts			X			X				Ethanolamide $H_2NCH(CH_3)CH_2OH$ $H_2NC(CH_3)(CH_2OH)_2$ $H_2NCH_2CH_2OH$ $(C_2H_5)_2N(CH_2CH_2OH)$ $HN(CH_2CH_2NH_2)CH_2CH_2OH$ $(CH_3)_2NCH_2CH_2OH$ $N(CH_2CH_2OH)_3$ - 552	
Isobutyl gallate			X			X				Citric acid - 139 Citric, tartaric or phosphoric acid - 562 Tartaric acid - 795	786, 896, 901
Isoamyl gallate						X		X		Citric or phosphoric acid - 562	1163
Oleylgallate						X					41

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Myristylgallate						X					41
Dodecylprotocatechoate						X					41
∝-Resorcylate						X					41
Isopropyl gallate						X					786
Gallanilide						X					744
E. Hydroquinone derivatives											
Tolu and chloro derivatives of hydroquinone									X		1101, 1110
Ethylhydroquinone						X					955
Propylhydroquinone						X					955
Monomethyl ether of hydroquinone			X			X				Vitamin B complex - 404	75, 937
Monobenzyl ether of hydroquinone	X					X		X	X		184, 209, 404, 895
Acetate of hydroquinone						X					404
Methylnaphthylhydroquinone						X					315

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Hydroquinone	X		X		X	X	X	X	X	Amino acid - 623 Citric acid - 574, 587, 1094 Methionine, ascorbic acid, leucine, trypsin hydrolysate of beef serum globulin - 214 Phosphoric acid - 179	51, 74 100, 112 123, 128 130, 131 133, 158 170, 185 238, 343 351, 360 395, 417 434, 454 485, 470 501, 526 562, 528 573, 577 606, 624 634, 683 703, 740 744, 745 781, 805 833, 864 900, 901 903, 904 905, 909 912, 923 934, 955 982, 983 1021, 1027 1029, 1036 1044, 1097 1101, 1107 1110, 1151 1163

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Toluhydroquinone						X	X			$Na_2S_2O_5$ - 1133	133
Trimethylhydroquinone						X					133
1,4-Naphthohydroquinone						X					133
Butylated hydroquinone monoalkyl ether and hydroquinone										Citric and ascorbic acids, H_3PO_4, ethyl acid phosphate or triethyl phosphate - 558	
Quinhydrone						X					1036
Monoethyl ether of hydroquinone			X								74
Thymolhydroquinone						X					901
Dimethyl ether of hydroquinone									X		1110
Polyhydroquinones									X		1110
3,4-Bis(2,5-dihydroxyphenyl) hexane			X								526
2-Isoamylhydroquinone			X								526
Alkyltocol						X					653

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Bis[bis(2-hydroxyethyl) aminomethyl] hydroquinoneoxalate	X	X		X					X		282
2,5-Bis[bis(2-hydroxyisopropyl) aminomethyl] hydroquinone	X	X		X					X		282
2-Methyl-3-phytyl-1,4-naphthohydroquinone				X				X			908
Di-t-butylhydroquinone									X		454
Butylated hydroquinone monoalkyl ether and propylgallate						X	X			Citric acid, phosphoric acid, ascorbic acid, ethyl acid phosphate - 85	
Isocoumarone						X					653
Hydroxycoumarone						X					653
β-Tocopherol			X			X			X	Lecithin - 171	469, 601 864, 999
γ-Tocopherol			X			X	X		X	Citric acid - 872 Lecithin - 171	469, 601 703, 864 999

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Tocopherol			X			X	X		X	Amino acid - 623 Ascorbic acid + p-aminobenzoic acid - 763 Ascorbyl monoester of fat acids and phospholipids - 860 Citric acid - 217 Citric and malonic acid - 49 Lecithin - 538, 956 Lecithin or phosphoric acid - 858	48, 249 287, 435 445, 489 521, 577 606, 653 741, 822 864, 939 1112, 1132
∝-Tocopherol			X			X	X		X	Ascorbic acid - 709 Ascorbic acid, threonine, tryptophan - 214 Ascorbyl monoester of a fatty acid - 859 Citric acid - 56, 260, 695, 710, 872 Lecithin - 171, 312 Leucine, tryptophan or ascorbate - 1028 $(NaPO_3)_6$ and Mandrell's salt - 586 1,4-Naphthohydroquinone - 387a	32, 112 116, 123 288, 315 406, 468 469, 537 540, 601 604, 703 729, 779 844, 848 864, 983 999, 1029 1151

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
										Phosphoric acid - 710 Vitamin B complex - 405	
α-Tocopherol with phytyl chain replaced by methyl							X				617
Diresorcinyltocol							X				617
β-Tocopherol (8-methyltocol)			X			X			X		80, 601, 615, 864, 999
2,3,4,6,7-Pentamethyl-5-hydroxycoumaran											973
2,4,6,7-Tetramethyl-3-ethyl-5-hydroxycoumaran											973
Subst. chroman											973
α-Tocopherol phosphate									X		467
Di- α-tocopherol							X				848
6-Hydroxychroman derivatives											489
o-Alkyl-p-alkoxyphenols		X									878

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
6-Hydroxy-2,2,5,7,8-pentamethylchroman						X				Citric and malonic acids - 577	
7-Methoxy-3-(3'-methoxy-4'-phenylmethoxy) benzilidinechromanone						X					744
Alkylaromaticdiethers (o-t-butyl-p-methoxy-phenylbutyl ether)				X							987
p-Hydroxycoumarans (2,2-dimethyl-6-t-butyl-5-hydroxy-coumaran)		X				X	X				382, 584
p-Hydroxychromans (2,2-dimethyl-6-hydroxychroman)		X				X					382
3-t-Butyl-4-hydroxy-anisole						X					291, 562
2-t-Alkyl-4-alkoxy-phenol						X					883
2-t-Butyl-4-hydroxy-anisole						X					291

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Cond. prod. of subst. p-hydroxyanisole and mono-t-butyl-p-cresol						X					938
F. Quinone derivatives											
Chroman-5,6-quinone						X					653
1,4-Naphthoquinone							X			$Na_2S_2O_5$ - 1133	
2-Nitrophenanthrene-quinone						X					1036
4-Nitrophenanthrene-quinone						X					1036
2,7-Dinitrophenan-threnequinone						X					1036
Vitamin K						X					315
Tetrahydropolycyclic-quinones (4a,5,8,8a-tetrahydro-1,4-naphthoquinone)	X										922, 923
4a,5,8,8a-Tetrahydro-1,4-naphthoquinone	X										124
6-Methyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone	X										124

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
5,5-Dimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone	X										124
5-Methyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone	X										124
5-Phenyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone	X										124
G. Miscellaneous phenolic compounds											
Calcium, sodium or aluminum lauryl phenoxide				X						Diethyl, dibutyl, diamyl, tartrates; octyl or amyl lactate; triamyl citrate - 530	
Magnesium or sodium cetyl phenoxide				X						"	
Calcium diamyl phenoxide				X						"	
β-Naphthyl, phenyl-p-aminophenol				X							561

Table 1 (cont.)

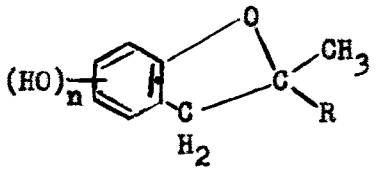
Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
1,5-Dihydroxynaphthalene						X	X				576, 577
2,4-Dimethyl-6-t-octylphenol				X							627, 628
Calcium cetylphenate											264
Salicylic acid alkyl esters (calcium salt)				X						Tertiary alkyl phenol sulfides - 333	331, 332
Sulfonamido-phenol or naphthol (5-(p-toluenesulfonamido)-1-naphthol)	X	X		X							361, 362
	X										370
1-[(p-4-morpholinylphenyl) methyl]-2-naphthol	X										422
5,8-Dihydro-1,2 (or 1,4)-dihydroxynaphthalene											801

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Polyhydric phenols		X		X		X		X	X	Reac. prod. of olefin and phosphorus sulfide - 869	795
HOArN=NArOH	X	X									808
Morpholinomethyl-β-naphthol				X							82
Bis(piperidinomethyl)-p-t-amylphenol				X							82
Alkylated phenol		X	X	X		X			X	Metal aliphatic polycarboxylate - 322	112, 327, 629, 885, 1008, 1093
Phenol branch chain alkyl ethers				X		X		X			994, 1121
Alkenyl subst. polyhydroxybenzene monoether	X										372
Alkylated salicylic acid				X						Amino phenols, phenylamine, diphenylamine, naphthylamines, phenylenediamines - 1122	

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
m-Hydroxybenzoic acid				X						Amino phenols, phenylamine, diphenylamine, naphthylamines, phenylenediamines - 1122	
Diisobutyl-β,β-hydroxynaphthoic acid				X						"	
Stannous salts of cardanol				X							797, 1116 1117
2,4-Dimethyl-6-t-butylphenol		X				X			X	Alkylated succinic acid or monocarboxylic acid with activating group α or β to CO_2H - 1162 N,N'-dibutylphenylenediamine - 1115	509, 629 885, 1042
2,4-Bis(p-tolylsulfonamido) phenol	X										1081
o-(p-Tolylsulfonamido) phenol	X										1081
p-(2-Naphthylsulfonamido) phenol	X										1081

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
p-(p-Tolylsulfonamido) phenol	X										1081
5-(p-Tolylsulfonamido)-1-naphthol	X										1081
Reac. prod. of alkylated aromatic hydroxy comp. and aldehyde-ammonia comp.				X							789
Vanilline (3,4,1) /$CH_3OC_6H_3(OH)CHO$/								X			108
Coumarin and hydroxy derivatives			X					X			292, 108 532
Salicylaldoxime						X					955
α-Naphthol			X		X	X			X		112, 131 133, 346 351, 614 746, 781 909, 912 1029
β-Naphthol			X		X	X			X		112, 133 344, 345 485, 632 781, 909 912

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Thymol						X			X		410, 632, 781
Chloromethylphenols				X							985
t-Alkyl ethers of naphthols				X		X					988, 1123
Phenol				X					X		33, 280, 1110
Diisopropylsalicylic acid (zinc or zinc-calcium salts)				X							1095
Phenol S (isopropylcresol)									X		170
Copper phenolate									X		1143
p-Hydroxydiphenylphenol								X			417
Cond. prod. of p-cresol and t-olefins or alcohols				X							986
2-t-butyl-4-methylphenol		X									629
2,4-Dimethylphenol		X									629
Phloroglucinol				X	X	X					593, 744, 909

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Aromatic p-hydroxymonobasic acid (propyl-, butyl- and benzylhydroxybenzoates) (p-hydroxybenzoic acid)							X			Aliphatic hydroxypolybasic acid (tartaric, citric, malic) - 813	897
Picric acid					X						909
Tricresol					X						909
m-Nitro-p-cresol					X						909
Kamala dye			X			X				Citric and tartaric acids - 274 Maleic acid, hydroquinone, oleic acid - 833	
Tumeric dye						X					833
Cresol									X		377
o-t-Butylphenol									X		377
2,4-Di-t-butylphenol									X		377
2,6-Di-t-butylphenol				X							1009

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
2,6-Di-t-butyl-p-cresol (ionol)	X	X		X	X	X	X	X	X		52, 87, 219, 253, 345, 457, 512, 530, 562, 584, 634, 639, 703, 756, 782, 822, 845, 924, 925, 934, 975, 1008, 1025
Butylated hydroxy-anisole						X	X	X	X	Acids, hydroquinone, lecithin, thiodipropionic acid - 560 Citric acid - 260, 900 $(NaPO_3)_6$ and Mandrell's salt - 189, 586, 703 Propylgallate and citric acid - 190, 292, 546 Propylgallate, citric acid and lecithin - 293	97, 190, 251, 292, 345, 431, 439, 551, 583, 603, 607, 634, 637, 638, 735, 756, 894, 1028, 1094, 1163
Polyalkylbenzylphenols				X							845

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
2,2',3,3'-Tetrahydroxybiphenyls (5,5'-dimethyl-2,2'-3,3'-tetrahydroxybiphenyl, also the 5,5'-dipropyl and the 5,5'-diamyl)						X					36, 194
Bis(2-hydroxy-3,5-dimethylphenyl) butane	X										146
Bis(4-hydroxy-2,5-dimethylphenyl) butane	X										146
o-Alkylhydroxyphenylalkanes	X										147
Reac. prod. of β-dihydroxy alcohols with phenols	X										124
2,4-Dihydroxybenzaldehyde		X		X				X	X	P_2S_5 isobutylene reac. prod. - 869	
p-Methoxyphenol						X					133
Cond. prod. of heterocyclichydroxyaromatic compds. and aldehyde and nitrogen compd.		X		X							767

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Bis(2-hydroxy-2-t-butyl-5-methylphenyl) furylmethane		X		X		X					1001
Bis(2-hydroxy-5-t-butylphenyl) furylmethane		X		X		X					1001
3,3',5,5'-Tetraalkyl-4,4'-dihydroxybiphenyl		X									255
N-(hydroxyaryl) pyrroles (N-(p-hydroxyphenyl)-2,5-dimethylpyrrole)	X			X		X			X		1091
4-Alkylphenylsallicylate									X		997
Cond. prod. of polyhydric phenol with vinyl aromatic compd.	X										125
Nitrated hydrogenated cardanol											252
Nitrogen-contg. derivative of 3-pentadecylphenol											429
Antimonyl derivative of polyhydric phenols	X			X					X		480

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Melilotin			X								538
Phenylmethylguaethol			X								538
2-Alkyl-4-methylphenol	X										545
Metal salts of alkyl-sulfoalkenylphenol (barium diamyl-(2,3-epithio-2-methyl-propyl) phenoxide)				X							770
2-t-Butyl-4-methoxy-phenol			X			X					112, 883
2,4-Dimethyl-6-t-octylphenol				X							256
Diamyl (sulfomethallyl) phenol or barium salt				X							769
Barium salt of paraffin wax methallyl-phenol				X							769
Reac. prod. of ∝-ethylhexanole and 2,4- and, or 2,5-dimethyl-phenol	X										433
p-Cresol									X		1124

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
1-(p-Hydroxyphenyl)-2,5-dimethylpyrrolidine				X							204
1-(p-hydroxyphenyl)-2,5-dimethyl-3-pyrroline				X							204
Mono-t-butylmethylphenol									X		345, 346
o-$HOC_6H_4CH:NC_2H_4NHCH_2OH$	X					X		X	X		257
Cond. prod. of polyhydric phenols and polyhydric alcohols	X	X				X		X	X		126
2,2-Bis(4-hydroxyphenyl) propane	X	X		X	X	X			X		1055
Reac. prod. of phenols with terpenes as nuclear substituents	X										542, 544 758
Hydrogenated 2,6-di-t-butyl-4-methylphenol		X		X							1145
3,4-Bis(m,p-dihydroxyphenyl)-n-hexane											1026
Alkylated cresylic acids	X										958

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Reac. prod. of butyl-p-cresol with an aldehyde (bis(2-hydroxy-3-butyl-5-methylphenyl) methane)				X							1003
2,6-Bis(4-hydroxy-2-methyl-5-isopropyl-benzoyl) hexestrol										Hydroquinone - 740	
Diamylphenol	X								X		639
1-Hydroxynaphthalene alkanoic acids											168
Reac. prod. of phenol-aldehyde resins with α,β-alkyleneoxides				X							401
Alkylated hydroxy-phenylmethyl or ethyl ether, p-dihydric-phenols or alkylgallic acid esters						X				Citric and tartaric acid - 636	
2,4,6-Trimethylphenol									X		1042
Bis(hydroxyalkoxy-phenyl) alkanes	X			X	X	X		X			1164

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Reac. prod. of phenols and salts of fatty acids (α-naphthol and stannous stearate)					X				X		1
Sn or Sb salts of phenolaldehyde or phenolketone reac. prods.	X										12
6,6'-Methylene-bis(2-isobornyl-4-methylphenol)	X	X		X		X		X			758, 1086
2,6-Bis-(4-hydroxy-3-methylbenzyl)-p-cresol			X								527
2,6-Bis-(4-hydroxy-2-methyl-5-isopropylbenzyl)-p-cresol			X								527
Mixture of 4,6-dimethyl-ol-o-cresol and p-cresol			X								527
2,3-Bis-(p-hydroxyphenyl)-2-butene			X								527
2,3-Bis-(4-hydroxy-3-methylphenyl) butane			X								527

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
2,2-Bis-(4-hydroxy-5-methylphenyl) propane								X			183
2,5-Dihydroxyphenyldimethylcarbinol						X					94
2,4-Bis-(2,5-dihydroxyphenyl)-4-methyl-2-pentene						X					94
Mercaptols and phenols (2,2-bis(p-hydroxyphenyl) propane)											630
Aliphatic aldehyde and monoalkyl-m-cresol	X										23
Olefin alkylated cresylic acid and alkyl halide	X										543
1-(2,5-Dimethoxyphenyl)-2-bromopropane						X					936
1,4-Bis-(2,5-dimethoxyphenyl)-2,3-dimethylbutane						X					936
1,4-Bis-(2,5-dihydroxyphenyl)-2,3-dimethylbutane (also tetraacetate)						X					936

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
3,4-Bis-(2,5-dimethoxy-phenyl) hexane						X					936
3,4-Bis-(2,5-dihydroxy-phenyl) hexane (also tetraacetate)						X					936
1-Ethyl-1-(p-hydroxy-phenyl)-2-methyl-6-indanol						X					936
Tin complexes of phenols	X										14
p-Octylphenol	X								X		1107
Menthylphenol	X								X		1107
2,2',3,3'-Biphenyl-tetrol						X					209
5,5'-Diacetyl-3,3'-di-methoxy-2,2'-biphenol						X					209
6,6'-Dihydroxy-5,5'-dimethoxy-3,3'-bi-phenyldicarboxaldehyde						X					209
5,5'-Diethyl-3,3'-di-methoxy-2,2'-biphenol						X					209
5,5'-Diethyl-2,2',3,3'-biphenyltetrol						X					209

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
3,3'-Dimethoxy-2,2',5-5'-biphenyltetrol						X					209
5,5'-Dimethyl-2,2',3,3'-biphenyltetrol						X				Citric acid - 209	
2,6-Di-t-butyl-4-butylphenol				X							1120
Butylated polyhydroxy-phenol	X										96
p-t-Amylphenol	X										96
2,6-Dichlorophenol indophenol						X					744
Di- and polyhydric phenols with hydroxyl in the o and p position						X					744
Cond. prod. of olefins and acid oils from cracked naphtha				X							1099
Bis-(3-t-butyl-5-methyl-2-hydroxy-phenyl) methane	X										934
Methylenedi-2-naphthol (WBC)	X										87

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
2,2'-Methylenebis-(4-methyl-6-t-butyl-phenol)(No. 2,2,4,6)	X								X		87, 756
2- or 3-Isobutyl-4-methoxyphenol						X					1069
1,2-Dialkoxybenzenes				X							457
Aroxyepoxyalkanes (1,2-epoxy-3-phenoxy-propane)				X							235
Alkylated phenol-aldehyde condensate and metal salts				X							647, 972
Reac. prod. of conjugated diolefin and polyhydric phenol	X										34
p-Alkoxyphenols (2-t-butyl-4-methoxy-phenol)	X			X						Mercaptoalkanoic acid (2-mercapto-ethanoic acid) - 1166	
Polyaralkylated phenols	X										533
Alkyl derivatives of p-alkoxyphenols							X				880

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Cond. prod. of 2-t-butyl-4-methylphenol with acetone (2,2'-bis-(2-hydroxy-3-t-butyl-5-methylphenyl) propane)	X										1165
Aralkylated hydroxybiphenyl (2-hydroxy-3-(α-methylbenzyl) biphenyl)									X		89
$3,4-(HO)_2C_6H_3CO_2R$						X					774
2,6-Dialkyl-4-alkoxyphenols		X				X			X		881
p-Nonylphenol						X		X			1161
o and p-Dodecylphenols						X		X			1161
6-t-Butyl-m-cresol						X		X			1161
2,3-Bis(hydroxybenzyl) butane						X					806
Aralkylated bisphenols	X		X	X		X		X			534
Cond. prod. of ketone and dihydroxydiphenylpropanes	X								X		1167

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
2,3,5,6-Tetraalkylated phenols									X		237
Cond. prod. of phenols with aromatic diolefins									X		773
t-Butyl-p-methoxyphenol									X		127
Dihydroxybiphenyl compds.									X		508
Coumarin						X					1027
6-Hydroxy-4-methyl-coumarin						X					1027
7-Hydroxy-4-methyl-coumarin						X					1027
7-Hydroxycoumarin						X					1027
5,7-Dihydroxy-4-methyl-coumarin						X					1027
Nitrogen compounds											
A. Amino phenol derivatives											
Bis(morpholinomethyl)-anilinomethylphenol				X							443

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Morpholinomethyl-bis-anilinomethylphenol				X							443
1-[(p-Dimethylamino-phenyl) methyl]-2-naphthol	X										422
2-Amino-5-hydroxy-toluene									X	Amines or inorganic hydroxides - 349	
p-Benzylaminophenol									X	"	1101
4-Butylaminophenol		X		X						Tripinene trithio-phosphite and di-salicylylidenepro-pylenediamine - 810 2-Mercapto-4-methylthiazole and disalicylylidene-propylenediamine - 810	512
Metol									X		430, 912
Cond. prod. of alde-hyde, polyamine and a hydroxy wax-subst. aromatic carboxylic acid		X		X							767

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Cond. prod. of aldehyde, polyamine and hydroxyaromatic compd.		X		X							768
Cond. prod. of aromatic amines and aliphatic ketones condensed with phenol and HCHO	X								X		492
4-Aminopentadecylphenol	X	X		X	X				X		251
Cond. prod. of dimethylaniline, HCHO and phenols				X							966
Di-subst. aminomethyldihydroxybenzene (2,5-bis(diethylaminomethyl) hydroquinone, 2-morpholinomethyl-4-methoxyphenol)		X		X	X	X			X		205
Calcium salt of reac. prod. of p-(tetramethylbutyl) phenol, aniline and HCHO				X							971
3'-Amino-4'-hydroxyflavonol			X								525

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
2-Amino-3-hydroxybenzoic acid or alkyl esters							X			Citric acid, phosphoric acid, phospholipids, ethylenediaminetetraacetic acid and its salts - 776	
1-Hydroxy-4-sec-butylamino-5,6,7,8-tetrahydronaphthalene		X				X					1056
N-sec-butyl-N-methyl-1-hydroxy-4-amino-5,6,7,8-tetrahydronaphthalene		X				X					1056
Hydroxyarylamine (N-(p-hydroxyphenyl)-p-phenylenediamine) (4-hydroxy-1-naphthylamine) (5-butylamino-1-naphthol-p-butylaminophenol) (p-isobutylaminophenol)	X	X					X	X		Esters of thioglycolic acid - 451	
p-Hydroxydiphenylamine									X		756

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
N-butyl-p-aminophenol	X	X		X			X	X		Benzyltrimethyl-ammonium butoxide - 206 Esters of thioglycolic acid - 451	
1-Hydroxy-4-sec-butylamino-5,8-dihydronaphthalene		X				X					1056
N-subst. aminophenols											1098
4-Aminocardanol		X		X							148, 1119
Isopropyl-p-aminophenol		X									899
o-Aminophenol									X		303
m-Aminophenol									X		303
Aminomethylphenols (3,3'-diallyl-5,5'-bis(dimethylaminomethyl)-4,4'-biphenol)									X		836
N-(4-hydroxybenzyl)-p-aminophenol		X									1059
N-(2-hydroxy-5-methylbenzyl) aminophenol		X									1059

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
N-(4-Aminobenzyl)-p-aminophenol		X									1059
N-alkyl-p-aminophenol		X									892
o-Hydroxy-R-CH:NR'-OH (o)											283a
Butyl-p-aminophenol		X									926, 1015
1,5-Aminonaphthol	X										16
2-(Dimethylamino-methyl)-4-aminophenol				X							811
8-Hydroxyquinoline						X					955
Aminophenols, phenylamine, diphenylamine, naphthylamines, phenylenediamines			X	X		X				Alkylated salicylic acid, m-hydroxybenzoic, diisobutyl-β,β-hydroxynaphthoic - 1122	112, 207
Primary or secondary aminophenol·HI or HBr		X									697
Benzyl-p-aminophenol		X		X							591, 592

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Dimethylaminomethyl-tridecylphenol				X							659
p-Aminophenol					X						335, 395, 417, 501
B. Amine derivatives											
N-phenyl-2-naphthyl-amine	X		X	X				X	X	Mercaptobenzoimid-azole - 579	7, 16, 238, 241, 344, 395, 417, 434, 539, 561, 569, 634, 658, 695, 867, 895, 934, 1107
Terpenylarylamine cond. prod. with an aldehyde	X										921
Terpenylarylamine cond. prod. with ketone	X										921
Aldol-α-naphthylamine petrolatum and di-phenylamine	X										696
RR'N-R"-CO-R"'											275

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Cond. prod. of ethyl or amyl aniline and formaldehyde and hydroxyaromatic compd.				X							352
Cond. prod. of diamylamine and acid aldehyde				X							352
N,N-dimethyl-p-phenylazoaniline							X				406
Imines from cond. of o-hydroxyaromatic aldehyde and primary alkylamine				X							198
Imines from cond. of o-hydroxyaromatic aldehyde and primary alkanolamine				X							198
Metal kelates of above two				X							47
Ar-NH-Ar-OCH_2-CR:CH_2 (4-methallyloxydiphenylamine)	X			X					X		368
5-Phenylamino-2,2-dimethyl-2,3-dihydrobenzofuran	X			X					X		368

Table 1 (cont.)

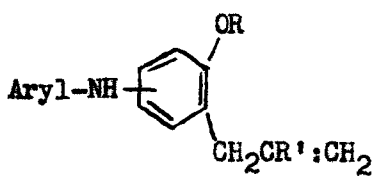
Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Diphenylamine	X					X		X	X	Vitamin B complex - 404	16, 335, 336, 346, 395, 417, 632, 658, 694, 805, 847, 1088, 1107
Subst. diphenylamine (alkyl group on one nucleus and amine group on the other) (4'-t-amyl-2,4-diaminodiphenylamine)	X	X		X		X		X	X	Dimethylamino-methylalkyl phenol - 310	376, 458
Ar-NH-arylene-N'-(R)SO_2-aryl	X	X		X		X	X		X		800
2-Amino-5-hydroxybiphenyl	X	X									554
R-N(X)-R'-N(A)R (A = hydroxyalkyl R' = arylene nucleus)	X										799
											369

Table 1 (cont.)

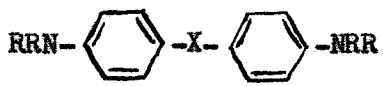
Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
											
(X = C,N,S,S-S,O,P,Al, B, As, Sb, O-P-O or O-Al-O)				X							165
p-Aminobenzoic acid			X								914
ArNH-Ar'-O-Y-COOX	X										424
Di-2-naphthyl-p-phenylenediamine	X								X		16, 395
Aniline									X		335
N-alkylanilines									X		335
Ethanolamine							X		X		469, 617, 844
Alkyl-subst. amino-arylhydroxide				X							469, 844
Triethanolamine						X		X			741, 1163
Benzylphenylamine				X					X		336, 1125
Tetramethyldiaminodi-phenylmethane				X							477

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Diaminodiphenylmethane				X							477
Alkyl-subst. aryloxy and arylthioxy amines				X							659
Phenylhydrazine									X		1101
α-Phenyl-α-methyl-hydrazine									X		1101
Reac. prod. of aliphatic ketone and aminofluorene or aminobenzofuran or aminocarbazole	X										491
Cond. prod. of aldehyde and polyalkyline-polyamine	X										787
Alkylene-subst. arylamine	X			X	X			X			475, 476, 950
N,N'-diphenylbenzidine	X									Secondary aromatic amine - 751	
5-Anilinoindane	X										371
Arylaminoarylidine carbonate	X										1090

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Mixture of alkylated diarylamine and prod. of cond. of conjugated diolefin with diarylamine	X				X		X				388, 389, 951
N,N'-dicycloaliphatic-p-phenylenediamine	X	X		X		X			X		233, 234
Triethylenetetramine	X										867
p-Phenylenediamine						X			X	Vitamin B complex - 404	238, 263, 163, 175, 430
N,N'-dibutyl-p-phenylenediamine		X								Cycloolefin - 1170 2,4-Dimethyl-6-t-butylphenol - 1115	1015
3-Methyallyl-4-methallyloxydiphenylamine	X										373
Cycloalkyloxydiarylamine	X										1082
4-Cyclohexyloxydiphenylamine	X										1082
N-(4-hexyloxyphenyl)-2-naphthylamine	X										1082

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
α-Naphthylamine	X										16, 912
Ammoniumaminosulfonic acids	X										16
m-Diaminoanisole	X										16
Reac. prod. of aromatic amines and 3-retenol	X			X							523
Hydroxyalkyl-subst. N,N'-diarylarylene-diamines	X										793
Methylanthranilate								X			1081
Reac. prod. of N,N'-diarylarylenediamine and olefin oxide	X										1083
4-Aminomethylacet-anilide				X							1127
m- or p-Aminoacet-anilide				X							1127
3-Diethylaminoacet-anilide				X							1127
Diphenylhydrazine						X					912
β-Naphthylamine						X					781

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
1,2-Dihydroquinoline and diarylamines (2,2,4-trimethyl-1,2-dihydroquinoline and diphenylamine)	X	X				X					374
p-Toluidine						X					280, 781
Arylaminoaryloxyaliphatic acids	X										1084
Cond. prod. of diarylamine and alkynes	X	X		X							952
Aniline				X	X				X		33, 280, 909
Mixture of t-alkylamines or alkylolamines and alkali or alkaline earth oil sol. sulfonic acids and "furfural bottoms"				X							247
p,p'-Diaminodiphenylmethane								X	X	Guanidine and quinine - 979	417
2,4-Tolylenediamine								X			417
N,N'-di-2-naphthyl-p-phenylenediamine	X							X			417, 639

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
o- and p-Ditolylamine								X			417
N-phenyl-1-naphthyl-amine	X		X					X	X		417, 658, 695, 998, 1107, 1142
N,N'-diphenylethylene-diamine								X			417
2,4-Diaminodiphenyl-amine								X			417
Cond. prod. of aniline and acetaldehyde								X			417
Cond. prod. of aniline and acetone								X			417
Cond. prod. of diphenyl-amine and acetone or glycolic aldehyde, gly-oxal, reducing sugars, hydroxyaldehydes and amino acid esters								X			417
Naphthylamine and aldol	X							X			241, 417, 565
(Aminomethyl)(acyl-amido) thiazoles		X		X							149

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Cond. prod. of primary aminoindan with a ketone	X										375
HN:C(NHR)R'			X			X					6
N,N'-diphenyl-p-phenylenediamine			X						X		279, 321, 583, 700, 1142
Methylaniline									X		321
Dimethylaniline									X		321
Ethylaniline									X		321
Benzylaniline											321
Dibenzylaniline											321
o-, m- and p-Nitroaniline					X						909
Benzidine		X						X			182, 340
Alkyl-subst. aryloxy- or arylmercapto-t-amines				X							661
Barium dimethylaminomethyltridecylphenol				X							661

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Acetaldehyde and α-naphthylamine											565
2,2,4-Trimethyl-6-phenyl-1,2-dihydroquinoline	X		X								7, 114, 934
Heptylated dimethylamine	X										7
Dimethylacridan	X										7
N,N'-dialkyl-p-phenylenediamine		X		X					X		892, 1105, 1125
$=NC_6H_4-X-C_6H_4N=$ (X is para to N= and is N,O,P,Al,B,As,Sb, S or no more than 2 carbons)						X				Alkylated succinic acid or monocarboxylic acid with activating group α or β to CO_2H - 1162	
Aromatic amine fat acid metal complex								X			1147
$HN:C(NHR)SO_2H$									X		1063

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Reac. prod. of aldehydes and aromatic amines (N,N'-diethyl-p,p'-diaminodiphenylmethane)	X			X					X		62
Reac. prod. of 3-retenol and m-phenylenediamine	X			X							522
Reac. prod. of 3-retenol and benzidine	X			X							522
Betaine osazone or salts or esters						X					929, 931
Betaine hydrazone or salts or esters						X					929
Betaine hydrazide or salts or esters						X					929, 931
Betaine amide or salts or esters						X					929, 931
o- or p-HOC_6H_4]$_2$p-$(CH_3)_2NC_6H_4$]$_2$CH				X							216
Isopropoxydiphenylamine								X			340

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Unsat. t-aliphatic amine (octa, decenyl, dimethylamine				X							63
RC(:NR")C(:NR")R (R = alkyl R" = subst. aromatic)							X				1154
p-Dimethylaminoaniline								X			340
p,p'-Diaminodiphenyl-sulfone								X			340
Ethyl-p-aminobenzoate								X			340
Guanidine-hydrochloride								X			340
Dimethylglyoxime								X			340
$(CH_3)_2C(NH_2)CH_2OH$								X			340
Isatin								X			340
Benzotriazole								X			340
Azoxybenzene								X			340
Benzoxazole								X			340
N,N'-disalicylidene-1,2-propanediamine									X		1128

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Cond. prod. of aniline and styrene and aliphatic ketone (2,2,4-trimethyl-6(1-phenylisopropyl)-1,2-dihydroquinoline)	X			X	X						390, 535
Cond. prod. of amines with N-subst. amino-aromatic aldehyde		X		X				X			1126
Reac. prod. of the reductive alkylation of isobutylenemethyl ketone	X			X	X				X		199
Cond. prod. of acetone and aniline									X		980
Cond. prod. of tris(2-aminoethyl) amine and β-diketones or hydroxymethylene ketones		X									418
Pentaerythritol tetramine with β-diketones and β-hydroxymethylene ketones (tetra(acetylacetone) pentaerythrityl-tetramine)									X		812

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
5-Pyrazolone derivatives	X				X						471
Cond. prod. of N-dimethylaniline and HCHO and benzylbenzoate				X							965
2-Amino-2-alkyl-N,N'-diaryl-1,3-propanediamine											505
Bis(diethylaminophenyl) methane				X						Alkylmaleic acid - 549 Dodecyl acid orthophosphate - 549	
Bis(isoamylaminophenyl) methane				X						"	
Bis(diamylaminophenyl) methane				X						"	
Bis(dimethylaminophenyl) methane				X						"	
Hydroxyarylalkylamine	X			X							692
C_6H_5N:PSCl				X							599
$CH_3O \cdot CO \cdot C_6H_4N$:PSCl				X							599

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
$C_6H_5N:PCl_3$				X							599
$ClC_6H_4N:PCl$				X							599
$(CH_3)_2C_6H_3N:PCl$				X							599
3,4-Benzopyrene											893
p-Methylaminoazobenzene											893
p-Aminoazobenzene											893
Bis(4-phenylaminophenyl) carbonate	X										1085
Bis(4-(2-naphthylamino) phenyl) carbonate	X										1085
Cond. prod. of benzaldehyde, dimethylamine and HCHO				X							968
Cond. prod. of dimethylamine and benzaldehyde				X							968
Cond. prod. of dimethylamine and 2,3-dimethoxybenzaldehyde				X							968

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Cond. prod. of 2,4-xylidine, N,N-dimethylaniline and HCHO				X							967
Reac. prod. of SO_2 with an amine									X		1052
t-Aminopolycarboxylic acids and salts									X		261
Alkyl-subst. amines											142
Alkylthienylketimine (N-phenyl-2-thienylmethylketimine)				X							427, 428
Prod. of reductive alkylation of p-phenylenediamine with a mixture of acetone and methylethyl ketone		X									479
Alkanedione dioximes (3-methyl-2,4-pentanedione dioxime)	X				X						536
Glucosamine							X				403
N,N'-diisopropyl-p-phenylenediamine and ketones		X									1104

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Tetraalkali, ammonium or amine salt of ethylenediaminetetra-acetic acid	X										868
Cond. prod. of halo-alkylthiophene and arylamines (N-(2-thenyl) aryl-amines)				X							667
Phenylethanolamine				X							994
Reac. prod. of pheno-thiazine, dimethyl-aniline and HCHO neutralized with cyclohexylamine				X							963
Mixture of hydrazine derivatives and ali-phatic acids									X		39
Reac. prod. of aldehyde and ammonia		X									203
Cond. prod. of o-hydroxyaromatic alde-hyde and aziridine	X										202
1-(p-Hydroxyphenyl)-4,4-dimethylpiperidine		X									911

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
N-/(trifluoromethyl) phenyl/-2-naphthylamine		X		X					X		975
Aliphatic ketone-aromatic amine cond. prod. mixed with 1,3-(2-benzothiazolylthio-methyl) urea	X										423
Cond. prod. of acetone and diphenylamine and hydroquinone	X										241
Subst. ethanolamines	X	X				X					448
Dialkylaminomethyl-phenols (Diamylaminomethyl-cardanol)		X									851
Ureides	X										4
Monooxalic acid salt of N,N'-di-sec-butyl-p-phenylenediamine	X										482, 483
Thiuronium base and phosphorous acids (Dodecylthiuronium salt of heptadecyl-hydroxyphenylmethyl-phosphonic acid)		X		X					X		688

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
o-Phenylenediamine	X										772
Trimethyldihydroquinoline polymer									X		998
Stannous complexes of primary, secondary or tertiary aromatic amines	X										15
4-Cyclohexylaminodiphenylamine		X									447
2,4-Bis(cyclohexylamino) diphenylamine		X									447
6,7-Dichloro-9-(1'-d-sorbityl) isoalloxazine											459
Hydrogenated quinoline	X	X		X		X		X	X	Aminophenol or other antioxidants - 507	
p-(Mono- and dihydroxyalkyl)) aminobenzoates									X		402
Hydroxy- and aminosubst. diphenylamine			X								114
Cyclohexylamine		X									1016

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
p-Subst. p-phenylene-diamine			X								114
Organic acid salt of 1-salicylideneaminoguani-dine				X							118
N-phenyl-N'-cyclohexyl-p-phenylenediamine	X										409
1-(p-Aminophenyl) hexa-methyleneimines		X									830
Mixture of N,N'-di-sec-butyl-p-phenylenedi-amine, N,N'-disalicyl-idene-1,2-diaminopro-pane and copper naphthenate		X									782
Aralkyl-subst. 1,2-dihydro-2,2-dialkyl-quinoline	X										490
N-(thienylalkyl) aryl-amines				X							662
N-isobutyl-N'-sec-butyl-p-phenylene-diamine	X	X									1106
Dinaphthylamine									X		658

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
N,N'-di-sec-butyl-p-phenylenediamine	X	X								Butylmercaptan and other mercaptans - 451	512, 934 1016
N,N'-bis(2,5-diamino-phenyl)-p-benzo-quinone diimine									X		50
N,N'-di-p-tolyl-2-amino-5-methyl-p-benzoquinone diimine									X		50
N-nitrosodiphenylamine		X		X							890
Ketone-diarylamine condensates	X			X							640, 641 642, 643
Metal salt of a mono-amide of 2,5-endo-ethylene $\Delta^{3,4}$ cyclo-hexene-1,6-dicarboxylic acid				X							698
Quaternary ammonium alkoxide (Benzyltrimethyl-ammonium butoxide)				X						N-butyl-p-amino-phenol - 206	
Versene								X			1163

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
1,4-Bis(sec-butylamino)-5,6,7,8-tetrahydro-naphthalene		X				X					1056
Urea-casein reac. prod.	X										412
Aliphatic ketone and diarylamine condensate and alkylated benzene	X										759
Anthraquinone diamine derivative								X			1163
1,4-Diamino-2,3,5,6-tetramethylbenzene and its alkylated and acetylated derivatives									X		237
2-Thiocyanato-4,6-diamino-s-triazine											874
N,N'-dialkyl-m-phenylenediamine		X							X		510
$RHNC_6H_4NO$ (R = alkyl or aralkyl)				X							355
N-aryltetrahydroquinoline				X							276
Procaine									X		141

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
p-Subst. arylamino-2,2,4-trialkyl-1,2-dihydroquinoline	X			X		X		X	X		803
Cinchona alkaloids	X										21
C. Guanidine derivatives											
Dicyanodiamide									X		470
1-Salicylalamino-guanidine	X					X	X		X		213
Biguanide								X		p-t-Amylphenyl-phosphate - 225	226
Biguanide-p-t-amyl-phenylphosphate								X			225
Phenylbiguanide								X			224
Phenylbiguanide hydro-chloride								X			224
Ethylolguanylurea				X				X			311
Reac. prod. of tri-phenylguanide, N-dimethylaniline and HCHO				X							962
o-Tolylbiguanide								X			1163

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Subst. biguanide salts of mercaptobenzo-thiazole								X			226
D. Amino acids											
Methionine						X				Gallic ester and an ester of benzoic, fumeric, tartaric, or citric acid - 415 Tocopherol, hydroquinone or NDGA - 623	649
Threonine										"	
Glycine						X	X			" H_3PO_4 and hydroxypolyoxyalkylene ester of fatty acid - 564 H_3PO_4 and a polyalkyleneoxide derivative of a fatty acid partial ester of a polyhydric alcohol or anhydride - 564 H_3PO_4 and sorbitan fatty acid ester - 564	939

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Phenylalanine										Gallic ester and an ester of benzoic, fumeric, tartaric, or citric acid - 415 Tocopherol, hydroquinone or NDGA - 623	
Arginine										"	
Tryptophan										"	
Tyrosine										"	
Butyltyrosine or alanine										"	
Leucine										Tocopherol, hydroquinone or NDGA - 623	
Norvaline										"	
Cysteine			X			X			X	"	57, 766, 822
Isoleucine								X		"	340
Proline						X				"	577
Valine										"	

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Glutamic acid										Tocopherol, hydroquinone or NDGA - 623	
Asparagine										"	
Norleucine										"	
Alanine										"	
N-(hydroxyaryl) aspartic acid diesters (diethyl-N-(p-hydroxyphenyl) aspartate)				X							341
Amino acids	X		X								20, 915
Polyethylenepolyaminoacid compds.											105
Aspartic acid						X		X			340, 555
Aminoacetic acid glycocol						X				$Na_4P_2O_7$ - 555	
p-Hydroxyphenylglycine									X		895
Thyroxine						X					744
Cystine			X			X				Water and Vitamin B complex - 404	766

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Glutathione						X					822
<u>Sulfur and nitrogen compounds</u>											
A. Thiosemicarbazide derivatives											
Phenylcarbazide		X							X		164
Diphenylcarbazide		X							X		164
o-Tolylcarbazide		X							X		164
1-Phenylsemicarbazide									X		1101
B. Vitamin B											
Vitamin B complex						X	X			α-Tocopherol - 405	1030
Thiamine (B_1)			X						X		365, 1064
C. Urea derivatives											
Thiourea					X	X			X	Sulfanilamide or sulfaguanidine and Vitamin B complex - 404	501, 683 726
Thiouracil										Water and Vitamin B complex - 404	

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Resins from bis(alkoxymethyl) ureas and polyhydroxyalkylamines	X								X		166
Methylene blue and urea									X		683
N,N-bis(p-dimethylaminophenyl) thiourea	X										449
N-phenyl-N'-(p-dimethylaminophenyl) thiourea	X										449
N-phenyl-N'-p-hydroxyphenylthiourea	X										449
N,N'-bis(p-hydroxyphenyl) thiourea	X										449
N,N'-diphenylthiourea	X										449
o-Phenylenethiourea	X										449, 450
N,N-bis(p-hydroxyphenyl) urea	X										449
N-phenyl-N'-p-hydroxyphenylurea	X										449
1,3-Bis(p-dimethylaminophenyl) thiourea	X										450

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
1,3-Diphenylthiourea	X										450
<u>Sulfur, selenium and tellurium compounds</u>											
A. Dithiocarbamate derivatives											
$RR'NCS_2NH_2RR'$ (preferably piperazine dithiocarbamate)		X		X							101
Zinc pentamethylenedithiocarbamate				X						Dicetyl sulfide - 265	
Benzyldibutyldithiocarbamate				X							886
Butyldibutyldithiocarbamate				X							886
Alkaline earth salt of monothiocarbamic acid, dithiocarbamic acid, or thiophosphocarbamic acid				X							886
Diisoamylammonium diisoamyldithiocarbamate				X							102

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Sodium diethyldithiocarbamate						X	X		X		795, 955 1066, 1067
N-cycloalkenyl carbamate (ethylcyclohexenyl carbamate) (cyclohexenylisocyanate)				X							918
N'-disubstituted thiocarbamyl sulfenamides		X									804
Sulfolanylcarbamate											717
Ethyl (2,2'-dihydroxyisopropyl) carbamate					X						453
Cyclic urethan corresponding to above					X						453
Sodium dialkyldithiocarbamates	X										295
Metal dithiocarbamates and other antioxidants	X										96
Nickle dibutyldithiocarbamate	X										819

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
B. Sulfide, selenide and telluride compounds											
Diethylsulfide									X		1014
Dimethylsulfide									X		1014
Diethercarboxylic acid alkarylsulfide				X							838
Diethercarboxylic acid alkarylselenide				X							838
Diethercarboxylic acid alkaryltelluride				X							838
2,4-Dialkyldiphenyl-monosulfide (alkaline earth salt)				X							229
Metal salts of phenyl-sulfides (magnesium salt of t-amylhydroxyphenyl-sulfide)				X							680, 701, 754
4,4'-Di-t-butyl- (or 4,4'-diamyl-) 2,2'-diaminodiphenyldi-sulfide											353

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
R-S-R (dioctyl, octyl, decyl, dodecyl, cetyl, cetyl propyl, etc.)										Organic P^{+5} compd. - 264	
Ether of sulfur, selenium or tellurium (cetylethylsulfide)										Organo-inorganic acid (calcium-cetyl phosphate) - 264	
Sulfopyridine		X									914
Hydroxysulfathiazole		X									914
Metal salts of alkylated hydroxyarylsulfides (Se or Te)				X							839
Sulfides of alkylated aryloxy carboxylic acid				X							840
Di-4-morpholine monosulfide				X							81
Dialkylmonohydric-phenolsulfides	X										88
Cetylselenide				X							266

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Cobalt di(2-t-amyl-4-hydroxyphenyl) sulfide	X										320
Calcium salt of reac. prod. of butene and phenol and PCl_3 reacted with ricinoleic acid followed by reac. with sulfur				X							961
Organic mono, di or polysulfide (dicetylsulfide)				X						Zinc pentamethylene dithiocarbamate - 265 Zinc salt of org. dithiocarbamic acid - 265	186
Sulfurized phenolic xanthates				X							663
Mercaptobenzothiazole and dimorpholine-polysulfide				X							83
Thio di-fat acids (β -dithiodipropionic and its esters diethyl, dioctyl and dilauryl)			X	X		X	X	X	X		583, 596, 778

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Cetyltelluride				X							266
Bis(chlorocetyl) selenide				X							266
Bis(hydroxycetyl) selenide				X							266
Dodecyldiselenide				X							266
Reac. prod. of multivalent metal salts of alkylated aromatic hydrocarbon with acidic functional groups and H_2S				X							843
Sulfurized cardinol ethers				X							788
Calcium salt of t-alkylhydroxyphenylsulfides				X						Isoalkyl ester of salicylic acid - 334	687
Sulfurized menthenes or menthadienes				X							550
Sulfurized cardinol				X							660
Dimethyldithiooxamide									X		1128

Table 1 (cont.)

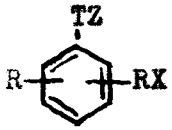
Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Alkylated hydroxyaryl or mercaptoaryl sulfides										Sulfurized oleic esters - 715	
Tin or triphenyltin or benzyltrimethylammonium salts of sulfurized unsat. carboxylic acid				X							598
 (T = oxygen, sulfur, selenium or tellurium Z = H, R, onium base or metal X = halogen, CN, SCN)	X					X		X	X		690
Sulfurized oleyl ester of oxalic acid				X							875
Metal salts of branched alkylphenolsulfides				X					X		677, 992
Sulfurized phenolic esters contg. halogen				X							601

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Reac. prod. of dialkylphenols and dialkylanilines with S_2Cl_2 or SCl_2 (2-hydroxy-3,5-di-t-amyl-4'-diethylaminodiphenyldisulfide)	X	X				X					227
Reac. prod. of sulfur, phosphorus or phosphorus sulfide with metal salts of phenols or aromatic mercaptans				X							990
Alkylhydroxyphenyldialkylaminophenylsulfides (2-hydroxy-3,5-di-t-amyl-4'-diethylaminodisulfide)	X	X		X		X					25
2,8-Dihydroxydibenzothiophene and t-amyl derivative				X							855
Dialkyl monoselenide				X							267
Dihexyl selenide				X							267
Dibenzyl monoselenide				X							267
Diallyl selenide				X							267

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Dialkyl monotelluride				X							267
Dicetyl telluride				X							267
Dilauryl telluride				X							267
Diparaffin telluride				X							267
(Amylmercapto) succinic acid								X			340
2-Mercaptobenzoxazole								X			340
Phenothioxin								X			340
Mercapto derivatives of dehydroabietic acid	X			X					X		825
β-Mercaptopropionic acid			X			X	X	X	X	Alkylated hydroxy-anisole and citric acid - 398 Alkylated hydroxy-anisole, tartaric acid, citric acid, glycerol, lecithin and ethyltyrosine - 399	396
$(CH_3N{:}NNH)_2S$							X				646
Alkylsulfenamides				X							452

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
2,3-Dimercaptopropanol									X		45, 46
Thioamides (thioacetamide)	X										472
Cond. prod. of aldehyde, polyamine and hydroxyaromatic compd. with P_2S_5, or S_2Cl_2, or S, or SCl_2, or PCl_3 and S_2Cl_2		X		X							768
Organic sulfhydryl compd. and a sulfide contg. an unsubst. amino group and 1% water							X				407
Cyclic mercaptans	X										581a
Tri-3-thienyltrithio-o-formate				X							152
Glyoxal-t-butylcresol cond. prods. and P_2S_5 or sulfur chloride				X							1002
Dibenzodimethylthiuram disulfide						X	X				1071
β-Alkylthioalkanone		X				X	X				1053

Table 1 (cont.)

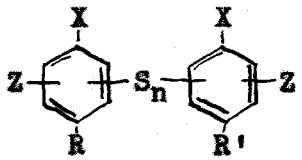
Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
 (Z = $CH(R_4)(NR_3R_2R_1X)$ X = hydroxyl group or an organic or inorganic acid radical) n = 1 to 4				X					X		298
H_2S and NH_4HS and oxygen contg. compds. (ketones, esters, acids, isophorone type fractions)				X							2
Bis(ketoalkyl) sulfide		X				X	X				200
Polymers of thiophene				X							503
Halogenated t-alkyl sulfides and polysulfides		X									299
Metal salts of aliphatic seleno- or telluromercaptans				X							1006, 1007
Esters of thiophenethiol				X							153
Bis(isooctylphenol) sulfide				X							969

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Reac. prod. of metal alkyl xanthate with amine salt of organic thiophosphoric or thiophosphorus acid				X							670
Aliphatic sulfide-sulfur and sulfide-selenium compds.				X							177
Didodecyl or dioctadecyl esters of thiopropionates									X		397
Aliphatic diselenides				X							268
2-Hydroxy-3-t-alkyl-5-methylbenzyl-t-alkyl sulfides				X							548
Dithiooxalodiamides and thioacetamides											588
Aliphatic thioethers of hydroquinone	X										757
Tetraalkyl- (aryl or aralkyl-) thiuramdisulfide						X	X				411, 752, 1066, 1067, 1068

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Tetramethylthiuram disulfide						X	X				1065, 1066 1067, 1071
Sulfurized aliphatic borates				X							876
Mercaptobenzothioxyl disulfide	X										978
Secondary and tertiary mercaptans and sulfides				X							93
Phenothiazine and derivatives	X			X						Diarylamine - 61 Phenolsulfide - 13	60, 539 734, 907 954, 974
Dialkylpolysulfides				X							633
4-(2,2-Dimethylpropyl)-1,2-dithio-4-cyclopentene-3-thione				X							1004
4-Methyl-5-t-butyl-1,2-dithia-4-cyclopentene-3-thione				X							1004
Alkyl derivative of thiophene and thiophene by-product tar						X					621

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Reac. prod. of thiophenes or alkylthiophenes with chlorinated paraffin waxes				X							842
3-Thienylpolysulfides				X							155
Dicarboxylic acid ester selenide or diselenide				X							178
Subst. sulfur hydrazides (RNHNH(X)R' X = SO_2, SO, SOS or S_2 or S_3)		X		X							932
1,1-Dicarboalkoxydiheptadecyl selenides				X							1005
H_2S or NH_4HS and unsat. cyclic ketones and PCl_5 or $POCl_3$	X			X							3
Thioether esters											242
Dialkylatedcresol sulfides	X										10
Mercaptoacetanilide derivatives											1136
3-Thienylthioalcohol				X							154

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
(Trifluoromethyl) phenothiazine		X		X							976
3-Isopropoxyphenothiazine		X		X							976
Benzophenothiazine carbonitrile		X		X							976
Bis(4-t-butyl-m-cresol) sulfide	X								X		639
Mixture of phenyl sulfide and Sb_2O_3	X										11
Metal salts of sulfonated ether of hydrogenated cardanol				X							1118
β-Alkylmercapto ketones, aldehydes or acids		X				X					1060
Di-t-alkylpolysulfides				X							300
Reac. prod. of bicyclic terpenes, P sulfides and alkylated phenols or alcohols and sulfur chlorides				X							1045
Penicillin			X								289

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
β -Alkyl and arylthio-alkanones						X					1051
Cond. prod. of arylsulfonic halide and alkali metal mercaptide				X							506
4,4'-Thiobis(6-t-butyl-m-cresol) (Santowhite)	X										87
(Carboxymethylthio) succinic acid						X					318
Cond. prod. of aldehyde or ketone with polyamine and P sulfide, S halide or S				X							5
1,2-Bis(ethylsulfinyl) ethane		X		X		X			X		1058
Sulfides of 3,6-dialkyl-subst. phenols (Thio-bis(3-methyl-6-t-dodecylphenol)	X										90
β ,β '-Thiodipropionic acid								X			1163
2,2'-Diaminodialkylsulfides									X		159

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
5-Nitro-2-thiophene-carboxamides											1153
Diamylmercaptodimethyl ether				X							705
Benzothiazole								X			340
Sulfanilamide				X							207
Phenoselenazine				X							907
Phenotellurazine				X							907
Barium salts of sulfurized alkylphenols		X									853
Mercaptopyrimidine								X			1011, 1046
Unsat. ethers of cyclic sulfides											591
Zinc isopropyl xanthate				X							668
C. Sulfoxide and sulfone type derivatives											
Dodecylselenoxide				X							266
Dodecylselenone				X							266
Phenylethyl sulfone				X							329

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Hydrocarbon-subst. thiacyclopentane-1,1-dioxide											716
Hydrocarbon-subst. thiacyclopentene-1,1-dioxide											716
Monochloro sulfones (3-chloro-2,4-di methylsulfolene)											719
Stannous bis(p-hydroxy-phenyl) sulfoxide	X										9
Subst. ethers of sulfolanes and sulfolenes											720
Ethyl-2-(ethylthio)-ethylsulfoxide		X		X		X			X		1058
Ethyl-2-(ethylthio)-ethylsulfone		X		X		X			X		1058
Ethyl-2-(ethylsulfonyl)-ethylsulfoxide		X		X		X			X		1058
β -Mercaptoketone and unsat. sulfoxide or sulfone = β -thiaketo-sulfoxides or sulfones				X		X					1057

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Alkaline earth salts of hydrocarbonsulfonic acid and organophosphoric acid				X							753
Arylaminoarylsulfonylamides (p-anilinobenzenesulfonylpiperidine)											802
Phosphorous and sulfur compounds											
A. Thiophosphoric acid type compounds											
Reac. prod. of bicyclicterpene and P_2S_5 mixed with alkylphenol or alcohol and SCl_2 and $CaCO_3$				X							815
Monocyclicterpenes and sulfur, then P_4S_3 or P_2S_5 or organic-subst. thiophosphoric acid				X							246, 541
Tetraphenol ester of thiophosphoric acid				X							561
(RO)(R'O)P(:S)SCu				X							678

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Heavy metal salt (barium preferable) of dicapryl ester of dithiophosphoric acid				X							229
Zinc salts of diamyldithiophosphate				X							229
Wax-subst. diaryl dithiophosphoric acids or salts				X							231
Bis(dihydroabietyl) dithiophosphate				X							230
Bis(tetrahydroabietyl) dithiophosphate				X							230
Reac. prod. of dioleyl ketone and P_2S_5				X							706
Multivalent metal salts of alkyl-subst. thiophosphoric acid				X							350, 913
Reac. prod. of terpene with P_2S_5				X						Ester of organic acid and wax-subst. hydroxyaromatic compd. - 354 Long chain alcohols and long chain fatty acids - 28	

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Reac. prod. of sulfurized oleyl ketone with P_2S_5				X							790
Complex dithiophosphoric acid esters				X							232
Alkylated hydroxyaromatic carboxylic acid and P_2S_5				X							367
Barium or tin salt of cardanyl thiophosphate				X							713
Cardanyl ester of thiophosphoric acid				X							713
P_2S_5 turpentine condensate and alkylphenols				X							655, 656
$S\langle SP(:S)(OC_6H_4C_8H_{17}\text{-}P)_2\rangle_2$				X							989
$S\langle SP(:S)(OC_6H_{11}Me\text{-}4)_2\rangle_2$				X							989
Metal salt of reac. prod. of phosphorous sulfide and oxygen-contg. wax				X							739
Cis-9-octadecen-1-ol and P_2S_5				X							103

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Pinene and P_2S_5				X						Ester of organic acid and wax-subst. hydroxyaromatic compd. - 354	103, 460
Diaryl sulfides (Se or Te) of alkyl-subst. diaryl dithiophosphoric acid or salt				X							841
Reac. prod. of oxidized petroleum wax and P_2S_5				X							365
Metal salts of reac. prod. of olefin and sulfur halide reacted with aromatic compd. followed by phosphorus and sulfur				X						Wool fat and sperm oil - 991	
P_2S_5 or P_2O_5 and unsat. cyclic ketone				X							392
Reac. prod. of metal alkylxanthate and metal thiophosphite or thiophosphate compds.	X			X							669
P sulfide and unsat. t-amine				X							67

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Reac. prod. of P_2S_5 and sulfurized unsat. acyclic ketone				X							791
Calcium salt of di-octyl-t-octylhydroxy-phenylmethyldithio-phosphate				X							993
Metal salts of phospho-sulfurized cond. prod. of a mercaptan and a carbonyl prod.				X							654
$(RO)_2PS_n(SS)S_nP(OR)_2$ (N = 0 or 1)				X							891
Selenophosphates				X							436
Metal salts of reac. prod. of P sulfides and organic amines or esters				X							66, 479
Barium salts of reac. prod. of P_2S_5 and high molecular weight ketone				X							478
Dialkyldithiophosphoric acid-formaldehyde cond. prods.				X							463, 465

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Calcium salts of aromatic methylene derivative of thiophosphoric acid				X							691
Reac. prod. of P_2S_5 and olefin	X	X		X	X	X		X	X		64, 66
Unsat. diesters of dithiophosphoric acid				X							40
P_2S_5 and phenolsulfonic acid											679
Reac. prod. of aliphatic nitrile and P sulfide				X							65
Triesters of dithiophosphoric acid				X							464
S-alkoxymethyl-O,O'-dialkyldithiophosphates											466
S-aminoalkyldithiophosphoric acid triesters											466
$[(RO)_2PS]_3P$				X				X	X		673
$[(RO)_2PS_2]_3P$				X				X	X		673

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
P_2S_5 and alkenylphosphate, thiophosphate or phosphite esters				X							771
S-hydroxybenzyl-O,O-dialkyldithiophosphoric acid triesters				X							228
Ether alcohol of cellosolve-type and P_2S_5 and HNO_2 = organodithiophosphoric acid disulfide				X							67[illegible]
P sulfide and hydrocarbon and zinc dithiocarbamate or guanidine carbonate				X							513
Esters of dithiophosphoric acid contg. terpene radicals											461
P_2S_5 and ester of unsat. polyhydric alcohols				X							70
Disulfide derivatives of organo-subst. thiophosphoric acids ($\angle(ROOC)_nR'O/_2P(:S)S_2$)				X							675

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Thialdine salt of organic thiophosphoric acids		X									674
Metal salt of P_2S_5 or P_4S_7 reacting with sat. aliphatic alcohol and sulfurized unsat. aliphatic alcohol				X							689
P sulfide and a polymer of an ester of α,β-unsat. dicarboxylic acid or a co-polymer of the ester with vinyl ester or vinyl aromatic hydrocarbon				X							69
S-(sulfurized terpene) dithiophosphoric acid triesters				X							462
Bicyclic terpene and P_2S_5 and S				X							91
<u>Phosphorus compounds</u>											
A. Phosphite esters											
Cetyltolylphosphite		X									408

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Tri-trialkanolamine phosphite				X							271
Tri-triethanolamine phosphite				X							271
Triethanoldiethylamine phosphite				X							271
Ditolyl monotriethanol-amine phosphite				X							271
Reac. prod. of hydroxy ester or acid with PCl_3				X							827
Thiodiglycol phosphite				X							595
RO(P)OR'(OR")	X										473
Triphenyl phosphite	X										473, 639, 888
Tri-o-tolyl phosphite	X										473
Tri-α-naphthyl phos-phite	X										473
Tri-p-phenoxyphenyl phosphite	X										473
Monododecyl phosphite									X		809

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Monobutylmonooctyl phosphite									X		809
Reac. prod. of dialkyl phosphites and quinones	X			X							571
Mixed anhydrides of organo-subst. phosphorus acids and carboxylic acids				X							671
PCl_3 and cyclohexanols											29
Fluoroalkanephosphonates											120
Mono or dialkyl esters of phosphonic acid or polymers	X										481
Reac. prod. of polyhalogenated quinones and trialkyl phosphites											572
PCl_3 + $CH_3CHOHCO_2H$ or its esters or salts				X							30
Benzenephosphonous acid									X		809
Aryl polyphosphites	X			X							755

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Organic phosphites and halogen compds.				X							254
HCHO and heterocyclic amine and hydroxyaromatic and PCl_3 (wax hydroxybenzylmorpholine and PCl_3)		X		X							768
B. Phosphate esters											
Chlororesorcinol phosphate				X							595
Biguanide-p-t-amylphenyl phosphate								X			224
Sodium-p-t-amyl phosphate								X			224
$(C_4H_9)_3PO_4$								X			340
Monophenyl phosphate									X		809
Fructose-6 phosphate							X				765
Organic seleno phosphate (triamylseleno phosphate)				X							1113
Didodecyl phosphate									X		809

Table 1 (cont.)

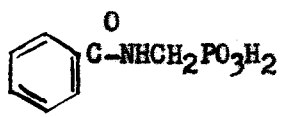
Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Neutral unsat. primary aliphatic amine salt of 3-methylbutyl-2-ethylhexyl-o-phosphoric acid				X							964
Monobutylmonodecyl phosphate									X		809
"Lorol" phosphate									X		809
									X		809
Phytic acid									X		809
C. Phosphatides											
Lecithin ($C_{42}H_{84}PO_9N$)			X	X		X	X		X		259, 274, 323, 445, 495, 521, 604, 606, 703, 809, 862, 872, 996, 1094
Phospholipids			X			X				Ascorbic monoesters of fatty acids - 861	1151
Cephelin							X		X		730, 809

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Prod. of lecithin and sulfur				X							610
Prod. of cephelin and sulfur				X							610
Reac. prod. of cephelin and 2-nitro-1-butanol				X							1077
Phosphatides treated with ammonia						X					749
Lecithin and conc. ammonia or corn oil phosphatide and conc. ammonia			X								175, 176
Phosphatides of soybean, corn and peanut oils						X					270
Phosphatidic acids from phosphatidyl cholines						X					270
Cadmium ppt. lecithin						X					316
Wheat germ phosphatides						X					826

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Organoarsenic compounds											
$PhNHAs(OCH_2Ph)_2$				X							92
1,5-Bis(dimethyl-arsenylpentane)				X							600
Diamylarsenic oxide or sulfide or disulfide				X							600
Triphenyl arsenite	X										474
$RAs(OH)_2O$		X									1074
Organoborn compounds											
$R_2B(OR')$ or $RB(OR')_2$				X							597
Wax phenyl borates				X							301
Dienols											
Dienols							X				100
Reductive acid							X				1034
Vitamin C and trimethylamine						X				Lecithin - 277	
Glyconoascorbic acid									X		920

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Ascorbic acid			X		X	X	X		X	Citric acid - 631, 887 Ethanolamine Heterocyclic oxygen compd. and P-NH_2 COOH Metaphosphoric acid, polybasic acids monobasic sat. fatty acids, aromatic carboxylic acids and mineral acids hydroxy acids and chlorine-subst. acetic acids (succinic malic citric acid) and sugars (sucrose fructose and glucose), thiourea and non-dialyzable group of natural prods. in citrus fruits - 488 NaCl and $Na_2S_2O_5$ + SO_2 - 504 NDGA - 1135 Sodium ascorbate and sucrose and nipagin - 281	27, 35 42, 57 79, 180 195, 236 328, 330 394, 456 518, 555 551, 646 649, 723 741, 747 748, 763 822, 831 850, 939 1011, 1032 1067, 1013 1101, 1102 1103, 1115 1146, 1150 1168

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
										Sucrose - 43 Quinone Tocopherol and hemoglobin, versene - 1130 Zinc chloride - 71	
Fatty acid monester of l-ascorbic acid							X			∝-Tocopherol ∝-Tocopherol (Vitamin E) or its isomers and analogues and phospholipids - 860 Benzoic, fumeric, tartaric or citric acid - 416 Phospholipids	414, 731 860, 863 859, 1023 1139
Fatty acid monoester of d-isoascorbic acid (d-isoascorbyl palmitate)					X		X				445, 455 741, 742 860, 862 956, 1023 1139, 1141
Ascorbic acid and hydroxycoumaran					X						653
d-Glucoascorbic acid							X				824, 1076

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Esters of ascorbic acid:											
Laurate					X						731, 1140
Myristate					X						731, 1140
Stearate			X		X						709, 730 1140
Caproate					X						1140
9,10-Dihydroxy-stearate					X						1140
l-Ascorbyl palmitate			X		X		X		X		414, 649 723, 731 864, 1140 1151, 1159
l-Ascorbic acid					X		X		X	Ethanolamine - 763 p-Aminobenzoic acid and caffeic acid - 764 p-Aminobenzoic acid and gallic acid - 764	78, 824 919, 920 1033, 1034 1076, 1092 1137, 1150
d-Isoascorbic acid			X				X		X		314, 824 943, 1033 1076, 1102 1168, 1169

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
d-Isoascorbyl monostearate					X						455, 742, 1141
d-Ascorbic acid									X		920, 1137
l-Araboascorbic acid									X		920
Reductone					X					p-Aminobenzoic acid and tocopherol - 763	
Dihydroxymaleic acid					X					"	
d-Isoascorbyl monolaurate					X						455, 1141
d-Isoascorbyl myristate					X						455, 1141
d-Isoascorbyl caproate						X					455
d-Isoascorbyl-~~o~~,i-dihydroxystearate						X					455
d-Araboascorbic acid											122
5,6-Diacetyl-l-ascorbic acid							X				1033
l-Gulosaccharo ascorbic acid											1075

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Organic acids											
Oxalic acid			X						X		683, 805 852, 1014
Phenylthioglycol-o-carboxylic acid									X		1014
Maleic acid						X	X				383, 437 529
Fumaric acid						X	X				437, 529
Citric acid and Na salt						X	X	X	X	Gum guaiac - 817	296, 297 555, 556 587, 604 606, 683 723, 730 756, 1069 1129, 1163
Alkylcarboxylate (or dithiocarboxyl or ether or a keto group or sulfur, selenium or tellurium analogue of either) subst. in α, β, γ alkyl position by Group Vb				X							322
Vanadyl oleyl phthalate				X							348

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Dihydroxytartaric acid or salts, esters or amides									X		1138
Dinitrotartaric acid or salts, esters or amides									X		1138
2-Ketogluconic acid											122
Vaccenic acid						X					315
Tartaric acid and Rochelle salts						X		X	X		296, 297 340, 683 723, 730
Pyruvic acid								X			340
Glycolic acid								X			340
Trichloropropionic acid								X			340
Tricarballylic acid						X					296, 297
Sodium acetate	X										978
Polyoxyethylene derivatives of stearic acid							X				169
Sodium nitrilotriacetate			X								915

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Sodium ethylenebis-(iminodiacetate)			X								915
Stannous alicyclic carboxylates (stannous rosinate and stannous naphthenates)	X										960
β -Stearoyloxytricarballylic acid						X					917
β -Palmitoylosytricarballylic acid						X					917
Dodecyl acid sulfate						X					270
Hexadecyl acid sulfate						X					270
Oxydialkanoic acids (oxydiacetic acid)						X					317
Tartaric acid									X		683
Esters											
Dimethyl maleate						X					529
Dimethyl fumerate						X					529
Distearyl maleate						X					529

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Dicyclohexyl tartrate				X							26
Diisopropyl tartrate				X							26
Dibutyl tartrate				X							26
Diisoamyl tartrate				X							26
Dibenzyl tartrate				X							26
Ethyl monobromoacetate and lithium carbonate and pyrogalline A								X			347
Monoaliphatic citrates (monoisopropyl citrate)						X					750, 1089
Di- or trialkyl or alkaline citrates						X					1089
Polyhydric alcohol stearate							X				169
Monoisopropyl citrate						X					1069
Cholesteryl oleate						X					315
Alcohols											
Acetylmethylcarbinol			X								946

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
m-Hydroxyacetophenone							X				100
Sorbitol						X					296, 297
Mannitol						X					296, 297
Vitamin A						X					315, 441, 442, 521, 882
Vitamin A acetate						X					315
Vitamin D						X	X			Lecithin - 277	939
Mixture of vitamins E and A						X					743
Terpineol									X		336
Geraniol									X		336
Vitamin P			X								736
Cond. prod. of 1-octadecanol and ethylene oxide	X										162
Dextrose								X			340
Benzoin						X					905
Benzyl alcohol									X		805

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Nuclear-subst. cinnamyl alcohols											19
Hydrocarbons and nitro and halo derivatives											
Decalin		X		X					X		561
β -Carotene						X					441, 442 1112
1,3-Diaryl-1,3-dialkyl cyclobutane	X										1080
Polymers of indene				X							977
Co-polymers of indene				X							977
2-Nitrofluorene		X									182
2,7-Dinitrofluorene		X									182
Dibiphenyleneethylene									X		1158
Hexadecane				X							33
Limonene								X		Citric acid - 290	
Anthracene									X		1124
Nitrobenzene											315

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Unsat. aliphatic hydrocarbons									X		1124
Diarylalkanes (1-p-tolyl-1-(2-methyl-5-ethylphenyl) ethane)				X							493
Cond. prod. of aromatic hydrocarbon and a di-halogenated hydro-carbon									X		221
Hydrocarbons									X		953
Inorganic compounds											
Ferrous sulfite									X		1014
Ferrous sulfide									X		1014
Sulfur				X		X			X		33, 107, 1014
Sodium thiosulfate	X	X	X		X		X	X	X	NaOH and sulfur - 676	646, 683, 805, 1014, 1163
$Na_2S_2O_4$									X		1014
Monobasic sodium phosphate							X				646

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Sodium nitrite							X				1031
Cyanide ion						X					955
Potassium (or ammonium) thiocyanate			X			X			X		253, 272 955
Sodium pyrophosphate						X	X				939, 1097
Phosphorous acid						X	X				606, 1097 1129
Ammonium sulfite							X				646
Potassium bisulfite							X				646
Tetramethylammonium bisulfite							X				646
Aluminum				X							33
Silver				X							33
Iron oxide				X							33
Carbon				X							33
Water				X							33
Stannous chloride				X							871

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Titannous chloride				X							871
Cupric ion				X							871
Phosphoric acid											723, 1129
Maddrell's salt											1129
Hexa meta phosphate											1129
Hepta phosphate											1129
Pyrophosphate											1129
Potassium iodide									X		17
Sulfur dioxide			X						X		391, 910
Potassium ferrocyanide			X								272
Sodium silicate								X			1163
Hydroxylamine	X								X		519, 683
Miscellaneous											
Montan wax									X		632, 1109
Petroleum residue asphalt									X		1108

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Gilsonite									X		1108
Manjak									X		1108
Ceresin									X		1108
Natural asphalt									X		1108
Fatty acid pitch									X		1108
Cottonseed pitch									X		1108
Stearin pitch									X		1108
Wheat germ oil			X			X	X			Citric acid and tartaric acid - 274	32, 171, 445, 521, 573, 606, 608
Vegetable oil						X					862, 1048
Distillate of destructively distilled ethanol extract of redwood				X							590
Methanol extract of oatmeal oil						X					277
Acetone extract of oatmeal oil						X					277, 1039

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Ethanol soln. of water extract of oatmeal						X					277
Unsaponifiable acetone extract of oatmeal oil						X					277
Oatmeal						X					1037
Timothy grass bacteria oil extracted		X		X		X			X		927, 930
Wood tars		X		X					X		359, 614, 619, 711, 1062
Gum guaiac	X	X		X	X	X	X	X	X	Monostearin or higher fatty alcohol or esters of monohydric and polyhydric alcohols and hydroxy-subst. amides - 157	445, 576, 577, 583, 604, 606, 615, 648, 699, 703, 741, 817, 905
Acyloxy and alkoxy derivatives of gum guaiac	X	X		X	X	X	X	X	X	"	121a
Rice bran extract							X			Hydroquinone - 406	798, 892
Peanut oil molecularly distilled						X					744, 779

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Extracts of:											
Soybean,	X		X			X					171, 172 173, 783
Wheatgerm,	X		X			X					171, 172 173, 783
Corngerm,			X								171, 172
Cottonseed,	X		X			X					172, 605 783
Oats, rye, olive, sesame, linseed, oiticita, and fish liver oils (cod, tuna and halibut)			X			X		X			172
Fat acid-betaine compds.											928
Corn extract (H_2O)							X		X		738, 1094
Oat extract (H_2O)			X				X		X		498, 738 1040, 1132
Blackstrap molasses methyl alcohol extract							X		X		737
Tannic acid or tannin						X	X				243, 577 591, 592 728, 896

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Purified redwood tannin		X		X							591, 592
Sweet potatoe tannin			X								760
Coffee tannin			X								760
Derivatives of amino-triphenylacetonitriles (3,3',3"-trichloro-4,4',4"-tris(dimethylamino) triphenylacetonitrile)	X					X	X				191
Cottonseed meal						X		X			468, 792
Wheatgerm meal						X					468
Extracts of unsaponifiable lipid fractions of dog liver, lung, kidney, spleen, adrenals, nerves, red corpuscles and serum, also mollusk and yeast			X								92
Tunafish liver antioxidant											286
Age Rite resin						X					741
Polymers of coumarone				X							977

Table 1 (cont.)

Type	Antioxidant for									A	Ref.
	R	G	C	L	P	E	F	S	M		
Co-polymers of coumarone				X							977
Hops							X				602
Fluorinated oil				X							363
Reac. prod. of ammonia, rosin and acetone or diacetone-alcohol or mesityloxide				X							38
Metal derivative of cashew nut oil				X							796
Steam distillate from cork			X								196
Extracts of brussel sprouts, green beans, squash, Irish potatoes, broccoli, cauliflower, cabbage, spinach, sweet potatoes, lettuce			X								837
Citrus fruit, parsley, haws, tomatoes, leeks			X								981
Water extract of beef liver						X					284

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Pea flour						X					555
Sucrose						X					555
Ether extract of oat flour						X					555
Reducible aniline dyes (thioninetoluidine blue, neutral red, phenosafranin, nile blue, thiosinamine-diethyl)					X						831
Human digestive enzymes (trypsin, pepsin, and clarase)										Citric acid - 217	
Hematochrome											442
Human serum albumin									X		58
Bovine serum albumin									X		58
Harvard serum protein fraction V									X		58
Dioxodisiloxane						X		X			197
2,4,6-Tri-t-butyl-cyclohexanone											1144

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Anise seed extract						X					518
Irish moss extract							X				1011
Pure vanilla concentrate							X				828
Viobin							X				728, 828
Rice oil extract			X								531, 761
Extract of ground nut oil											53
Palm oil antioxidants											287
Extract of unripe olive and leaves						X					902
Organic solvent extract of soap stock			X							Phosphatide - 174	
Seeds, grains, legumes, grasses, or extracts of same			X			X	X	X		Nicotinic acid or amide ester or salt - 1035	
Citrus peel, citrus pulp, and citrus albedo tissues						X				Lecithin or phosphoric acid - 821	

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Unsat. aldehydes with 5 conjugated double bonds (11-phenylhendeca-pentaenal, lactaro-violin, lycopinal)						X					1154
Cond. prod. of aliphatic nitrile with aromatic amine, phenol or hydrocarbon				X							594
Cyclohexanonebisulfite									X		440
Cereals						X	X				521, 708
Extract of creosote bush							X				935
$COCl_2$									X		612
Protein			X				X				56, 498, 1012
Antioxidant prepared from milk							X				949
Lactaroviolin							X				1155
Wood rosin extract											1061
1,2-Dinitroso compds.	X	X		X		X					879

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Methyl red	X										434
Soybean flour						X	X				308, 521, 792
Chlorinated cyclic polymers	X	X		X				X			721
Antioxidant prepared from whey							X				948, 1050
Dow-Corning-type 200 fluid $((CH_3)_3Si(OSi[CH_3]_2)_n-OSi(CH_3)_3)$								X			502
Organosilicon polymers				X							984
Aqueous extract of frozen snap beans			X								144
Unsaponifiable matter from camellia oil						X					762
2,4-Di-(trichloromethyl)-6-nitro-1,3-benzo-dioxane	X	X									1134
Extract of green chillies, garlic and onion											273

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Orange juice, lemon juice, sea buckthorn berry juice, sugar-contg. marmalades			X								915
Trilon B, Trilon A, Stabilisator A, pectin, sugar			X								915
Sustane						X	X				357, 439
Osage orange extract						X				Di- or tricarboxylic acids - 215	
Mixture of $NaHSO_3$, Na_2CO_3 and citric acid									X		31
C_2I_4									X		511
$C_2I_3NO_2$									X		511
Dry distillation fluid from Japanese cypress and cryptomeria			X			X					712
Posterior pituitary extract						X					744
Anterior pituitary extract						X					744

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Plantain						X					744
Tapioca flours						X					744
Ginger starch						X					744
Sesame oil						X					744
Cocoanut oil						X					744
Cacao shell, cacao powder, extract of cacao shell, extract of cacao powder							X				728
Spice extracts						X					211
Tenox II						X					393
Safflower flour						X					308
Fenugreek flour						X					308
Carol bean flour						X					308
Aureomycin			X								289
Neomycin			X								289
Cream, skim milk, fermented skim milk			X								710

Table 1 (cont.)

Type	Antioxidant for R	G	C	L	P	E	F	S	M	A	Ref.
Sulfhydryl substance in fruit			X								1171
Sodium alginate			X								312
Amines and phenols from branch chained olefin and p-cyclic disubst. benzene hydrocarbon (1-p-tolyl-1-(2-methyl-5-cyclohexyl-phenyl) cyclohexane)				X							494
Sustane 1F						X					1163
Sustane 3F						X					1163
2-Furfurylidenemalono-nitrile									X		432

EXPERIMENTAL

Separation and Identification of Products from the Air Oxidation Experiments

Materials and experimental procedure

Preparation of materials. Tetralin (Kodak practical grade) was washed with concentrated sulfuric acid until the acid layer showed no more red coloration, then washed with water, dried and distilled under 15 to 30 mm. pressure at 91°.

Diphenylamine (Matheson Co., Inc.) was recrystallized five or six times from Skelly D. M.p. was 54-55°.

Azo-bis-isobutyronitrile was prepared by the method of Thiele and Heuser[1049] as modified by Dox.[283b] The m.p. was 105-106°.

Chlorobenzene was redistilled, b.p. 130-131°.

Methacrylonitrile was washed with alkali, dried and distilled.

p,p'-Dihydroxyazobenzene, m.p. 215-216°, was prepared by the method of Atkinson, et. al.[37]

Preparation of phenazine and 9,10-dihydrophenazine was accomplished by the method of Ris.[865] The 9,10-dihydrophenazine was recrystallized from chlorobenzene after decolorizing the impure material with carbon black. The m.p. was 305-306° in a sealed tube under nitrogen, and 270° was obtained in an open tube. Literature reports 212° as the melting point. Some of the material was heated in air and a yellow material sublimed which melted at 169°. Phenazine melts at 169-172° according to the literature.

N,N'-diphenyl-p-phenylenediamine obtained from B. F. Goodrich was purified by five recrystallizations from chlorobenzene after the carbon

black was filtered off. M.p. was 147-149°.

N,N'-diphenylquinonediimine (benzoquinone dianil) was prepared by the method of Piccard[818] from N,N'-diphenyl-p-phenylenediamine by chromic acid oxidation. The product melted at 183.5° (literature 176-180°) after recrystallization from chlorobenzene.

Quinhydrone base from N,N'-diphenyl-p-phenylenediimine was prepared by the method of Piccard.[818] A light chocolate brown powder, m.p. 123-127° (literature 130-135°), was obtained.

Quinoneazine was prepared by the method of Willstatter and Benz.[1156] The crystals were orange-red. On being heated, the crystals darkened at 157-159° and on further heating turned red again at 200-203°. The crystals did not melt when heated to 300°. A flame test gave a sudden, rapid darkening and a burst of flame, then slow oxidation of the residue until it was all gone. On mixing a small amount of material in methylene chloride solution with p,p'-dihydroxyazobenzene, the quinhydrone-type material was obtained giving crystals which melted at 205° (pure material m.p. 185°). Since the material had the dark appearance of the complex and no careful preparation of a 1:1 ratio had been made, it was concluded that the quinoneazine had been prepared. (Other authors give the quinoneazine m.p. as 158° (see Hunter and Barnes[484]), while Bielstein[117] states that there are two crystalline forms, one dark red prisms, the other dark yellow needles. The latter mentions a darkening on heating and explosion at 158°.)

Preparation of phenylazotriphenylmethane was carried out by the method of Gomberg and Berger.[387b] In the first preparation the hydrazo compound did not dissolve readily in alcohol as the literature indicates, so methylene chloride was used to dissolve it. On cooling, beautiful yellow crystals

precipitated which had a m.p. of 114-116°. The literature warns that considerable contamination with the hydrazo compound had little effect on the m.p. as was later discovered in using this material. The yield was 55.72 g. The oxidation with N_2O_3 as Gomberg and Berger recommend was thus not performed.

A second preparation was performed using the same method to prepare the hydrazo compound. The oxidation which followed was according to the method of Cohen and Wang[218b] using hydrogen peroxide and bicarbonate solution to obtain the azo compound. The ether solution of the azo compound was separated, and the ether evaporated and a mixture of alcohol and methylene chloride was used as a recrystallization solvent. The crystals melted at 116-118°. It was noted that some were yellow and some tended to be white and that the yellow crystals melted first. Another recrystallization gave large clear yellow crystals and also small lighter colored ones, m.p. 115-118°. The yield was 59.97 g. or 48 percent. This material proved to be contaminated with hydrazo compound, as was the first, even though the reaction was carried on overnight, instead of five hours as recommended. The hydrogen peroxide may have deteriorated. Further purification was later commenced.

An attempt was made to use the method of Gomberg and Berger[387b] to prepare p-nitrophenylazotriphenylmethane from tritylchloride and p-nitrophenylhydrazine. The material which precipitated was not the hydrochloride of the hydrazine as anticipated, but was not very soluble in water, gave no precipitate with silver nitrate and melted at 175-180°. Two other attempts were made but met with no success.

Apparatus and procedures. A three-necked standard taper flask was equipped with a stopper, a tube with small holes on the end through which air could bubble, and a Friedrick condenser. Suction was applied to the top of the condenser causing air to bubble from the gas dispersing tube through the solution in the flask and out of the condenser. A drying tube was placed on the end of the air inlet bubbler tube to keep moisture out of the system. The three-necked flask was placed in a constant temperature bath and after the reaction mixture was homogeneous, the suction applied so that air bubbled slowly up through the solution.

Peroxide determinations were by the method of Hammond.[419]

Attempted separation and identification of products from air oxidation using diphenylamine as inhibitor

Air oxidations with tetralin as substrate. A mixture of 200 g. of tetralin (1.51 moles), 16.7 g. of diphenylamine (.0987 mole) and 15 g. (.0987 mole) of azo-bis-isobutyronitrile was placed in a 500 ml. round bottom flask and placed in the constant temperature bath as described above. The bath was maintained at approximately 75°. The reaction mixture turned brown within an hour and was black within four hours of reaction time. A great deal of work and time was spent in an effort to separate and identify the reaction products. The original reaction mixture was extracted with 2N sodium hydroxide, then with hydrochloric acid. Then followed various methods of separation. Steam distillation, distillation under reduced pressure, recrystallization, sublimation and chromatography were employed. Infrared spectra were used in an effort to establish something of the identity of many of the chromatographic fractions. Most of the

compounds were oily materials and no clean-cut separation was achieved by chromatography or the other methods, with the exception of recovering the starting materials, tetralin and diphenylamine, and the dimer, tetramethylsuccinonitrile, from the decomposition of the initiator. Work involving isolation of products from air oxidations with diphenylamine as an inhibitor was later abandoned in favor of inhibitors which exhibit the property of reacting with two peroxy radicals per molecule. From kinetic studies[136] it appears that many inhibitors exhibit small integral numbers (often two) as stoichiometric factors of peroxy radicals reacting with inhibitors. However, diphenylamine and its methoxy derivative prove to be anomolous in this respect showing a nonintegral stoichiometric factor, indicating that at least two reaction paths are probably being followed simultaneously. This being the case, inhibitors were subsequently chosen which gave the usual stoichiometric factor of two for the studies performed on reaction products of inhibited air oxidized systems.

A second oxidation with tetralin as substrate follows. A mixture of 100 g. (.755 mole) of tetralin, 8.35 g. (.04935 mole) of diphenylamine and 7.5 g. (.04935 mole) of azo-bis-isobutyronitrile was placed in a 500 ml. round bottom three neck flask and after the mixture was homogeneous the flask was placed in the water bath which was held at 62.2°. The experimental set up had been modified from the previous run in order to try to follow the uptake of oxygen. A stopper was placed in the top of the Friedrick condenser, a stirrer was placed in the middle neck and an oxygen delivery tube in the third neck. The oxygen delivery tube was connected to a tube reaching to the top of an inverted two liter graduate cylinder which was filled with oxygen. A slight pressure was maintained on the oxygen in

the cylinder by raising the leveling bulb, containing mineral oil, a small amount above the level in the cylinder. The whole system was previously flushed with oxygen before the reaction was started. The effort to determine oxygen uptake was not successful because of a leak around the stirrer. The accuracy of the method is also limited by the necessity of calculating the amount of nitrogen evolved during the run. This is almost equal to the oxygen absorbed, as later discovered.[420] After five days, another 7.5 g. (.04935 mole) of azo-bis-isobutyronitrile was added. The reaction was allowed to proceed for 24 days. The tetralin and tetramethylsuccinonitrile were removed from the reaction mixture by distillation under reduced pressure of 1 to 5 mm. through a four foot Oldershaw column. Because of the difficulty previously encountered in separating tetralin and tetramethylsuccinonitrile, it was decided to estimate the amount of the dinitrile in the tetralin by making standard solutions of a known amount of the solid material dissolved in a known volume of tetralin. This was done, but the infrared spectrum of the solutions did not lend itself to any quantitative results. The refractive index was also disappointing. However, it was possible to obtain a good estimate of the amount of the dinitrile present in tetralin saturated at 25° by placing the volumetric flasks in a 25° water bath overnight and weighing the excess crystals.

Since only a very small crystal was obtained from Sample #2, this was taken as being most accurate since there would be less tetralin adsorbed on this crystal than on the others.

Table 2

Ten ml. of tetralin and tetramethylsuccinonitrile mixture at 25°

Sample #	Beginning wt. of dinitrile	Wt. of dinitrile recovered	Wt. of dinitrile dissolved
1	0.9998 g.	0.5241 g.	0.4787 g.
2	0.5006 g.	0.00017 g.	0.5004 g.
3	0.2493 g.	----	----
4	0.1251 g.	----	----

By this means the total amount of dinitrile accounted for in saturated tetralin solution and from excess crystals amounted to 5.66 g. (.0435 mole) which is 44.1 percent of the total charge of the initiator azo-bis-isobutyronitrile. This is in substantial agreement with the findings of Hammond, Sen and Boozer[421] concerning the efficiency of radicals produced which initiate chains instead of dimerizing.

The residue from the distillation under reduced pressure was titrated by the method of Hammond[419] giving .0199 milliequivalents of peroxide per ml. With approximately 78 ml. of solution this gives a total of 0.78 millimoles of peroxide as compared to 108 millimoles of hydroperoxide theoretically possible, assuming 44 percent dimerization of the initiator radicals. This low result raised the possibility that the peroxide was so unstable it was being destroyed during removal of the solvent.

After the peroxide determination, the residue was dissolved in Skelly B and adsorbed on a chromatographic column of Al_2O_3. Numerous fractions were eluted but no products were isolated and identified other than diphenylamine. Infrared spectra were taken in numerous cases as an aid in

trying to differentiate and identify components in the varicolored oily fractions. The work on diphenylamine products was subsequently abandoned for the reasons given in the early part of this section.

Air oxidations with chlorobenzene as solvent. A mixture was made of 84.98 g. (.755 mole)(76.8 ml.) of chlorobenzene, 8.35 g. (.04935 mole) of diphenylamine and 7.5 g. (.04935 mole) of azo-bis-isobutyronitrile. The homogeneous mixture was placed in the water bath which was at 62.5°. Oxygen under slight pressure was placed over the stirred reaction mixture as in the previous run. After 128 hours (approximately 8 half lives of the initiator) the spent gases, mostly nitrogen, from the initiator were flushed out of the system and new oxygen was added along with another charge of 7.5 g. (.04935 mole) of azo-bis-isobutyronitrile.

A one ml. sample of the reaction mixture was titrated for peroxide by the method of Hammond[419] giving .02985 milliequivalents of peroxide per ml. of reaction mixture.

After a total time of 284 hours (156 hours and 9.8 half lives since the last charge of initiator) the run was stopped. Since the odor of hydrogen cyanide had been detected previously, some of the gas above the reaction mixture was passed through slightly acidified silver nitrate solution. A copious precipitate of silver cyanide was obtained.

Four one ml. samples were titrated for peroxide. The concentration was not over .0542 milliequivalents per ml. of reaction mixture. Assuming no loss of solvent (76.8 ml.), this corresponds to a total of 4 milliequivalents or 2 millimoles of hydroperoxide in the solution, compared to a total of approximately 108 millimoles of hydroperoxide theoretically possible,

assuming 44 percent of the initiator radicals formed dimers as shown in the previous experiment. This indicated that the low peroxide content was not primarily a result of separation procedures. After considerable effort to isolate products, the work on diphenylamine products was ceased for the reasons previously given.

Air oxidation of azo-bis-isobutyronitrile

A mixture of 15 g. (.0987 mole) of azo-bis-isobutyronitrile and 85 g. (.755 mole)(76.8 ml.) of chlorobenzene was placed in a three-necked round bottom flask, which was, upon dissolving the initiator, immersed in a water bath at 62.2°. Oxygen under slight pressure was maintained over the stirred reaction mixture as in the previous experiment. The increase in the peroxide content was followed at intervals during the run (144.5 hours). It was noted that the determination of peroxide content gave results approximately twice as great when hydrogen chloride was used along with acetic acid to catalyse the formation of iodine from iodide ion as when no strong acid was used. This is assumed to be a possible indication of the presence of peroxide and a more unstable hydroperoxide. The final reading with hydrogen chloride catalyst was .0873 milliequivalents of peroxide per ml. or 6.74 total milliequivalents based on starting volume assuming no change in concentration during the run (only 3.8 ml. of solvent were unaccounted for after the solvent was removed under vacuum). Taking into account the efficiency of initiation[421] and assuming all that was formed was hydroperoxide, only 2.62 percent of the material formed stable hydroperoxide. Assuming all the material formed was peroxide, the percentage would be 5.24. At the end of the run the gas above the reaction mixture was drawn into

aqueous silver nitrate, from which silver cyanide precipitated copiously. Attempts to isolate other products by fractional recrystallizations and solvent extractions using petroleum ether, methylene chloride, alcohol and various solvent mixtures led to the isolation of only tetramethylsuccinonitrile and a white amorphous solid. The latter showed strong infrared absorption at 2240, 1740 and 1680 cm^{-1} and appeared to have a spectrum similar to polymethacrylonitrile.

Air oxidation of methacrylonitrile

A mixture of 33.55 g. (.5 mole) of methacrylonitrile, 423 g. of chlorobenzene and 15 g. (.0987 mole) of azo-bis-isobutyronitrile was placed in a one liter, three-necked round bottom flask. After dissolution of the initiator, the flask was placed in a water bath at 62.2°. Oxygen was slowly bubbled through the solution. After 74 hours the oxygen was turned off. During the run the concentration of hydroperoxide steadily increased to about .217 milliequivalents per ml. Since about 400 ml. of solvent was recovered on distillation under reduced pressure, the total concentration of hydroperoxide was 46.8 millimoles. This concentration fell to .169 milliequivalents per ml. as the reaction mixture was allowed to stand at room temperature for a week before distillation. After distillation at 41° and 45 mm. a viscous orange residue remained which weighed 34.9 g. Hydrogen cyanide was again detected in the gases above the reaction mixture.

Separation and identification of products from air oxidations with N,N'-diphenyl-p-phenylenediamine as inhibitor

Isolation of N,N'-diphenylquinonediimine. A mixture of 3.75 g. (.02467 mole) of azo-bis-isobutyronitrile, 2.485 g. (.00957 mole) of N,N'-diphenyl-p-phenylenediamine and 200 ml. of chlorobenzene in a round bottom three-necked flask equipped as in the first oxidation run was placed in a water bath maintained at 62.2°. The light yellow solution turned brown in five minutes and was red at the end of the run. Oxygen was bubbled through the solution for 8 half lives of the initiator (96 hours). Cooling overnight in the refrigerator produced no solid crystals so the chlorobenzene was removed from the reaction mixture by distillation at 50 mm. and 40°. A small amount of polymeric solid (polymethacrylonitrile) was observed on the side of the reaction vessel.

After the distillation the solid material in the residue was filtered off and the remaining chlorobenzene removed by evaporation with a stream of air. The solid material which was filtered off was extracted with one part methylene chloride and 40 parts Skelly D to remove the dinitrile. After the extraction, the remaining solid was recrystallized from methylene chloride. A fraction weighing 0.35 g. gave a m.p. of 183-185° and a mixed melting point with previously prepared N,N'-diphenylquinonediimine (m.p. 183.5) gave a melting point of 184.5-188°. Other fractions, not quite so pure, brought the total weight to 1.14 g., a yield of approximately 46 percent. The product, which one could observe in other fractions along with a dark viscous material, was never separated, but seemed to decompose on repeated attempts at purification. This may not be surprising since

Tulagin[1078] remarks that quinonimine dyes are unstable to light, acids and alkalies. The spectra of two of the worst fractions were taken in the ultraviolet and visible regions with a Beckman Model DU spectrophotometer. One gave a minimum at 265 mμ and a maximum at 293 mμ, the other gave a minimum at 250 mμ and a maximum at 295 mμ. These have little resemblance to the spectra of N,N'-diphenyl-p-phenylenediimine. Another spectrum was taken of a grey amorphous product which precipitated from all the fractions with addition of Skelly B to the methylene chloride solutions. Minima at 300 and 340 mμ and maxima at 305 and 350 mμ were obtained.

Spectra of N,N'-diphenyl-p-phenylenediamine and its derivatives in methanol. The following solutions were made:

.000030 g./ml. of N,N'-diphenyl-p-phenylenediamine,

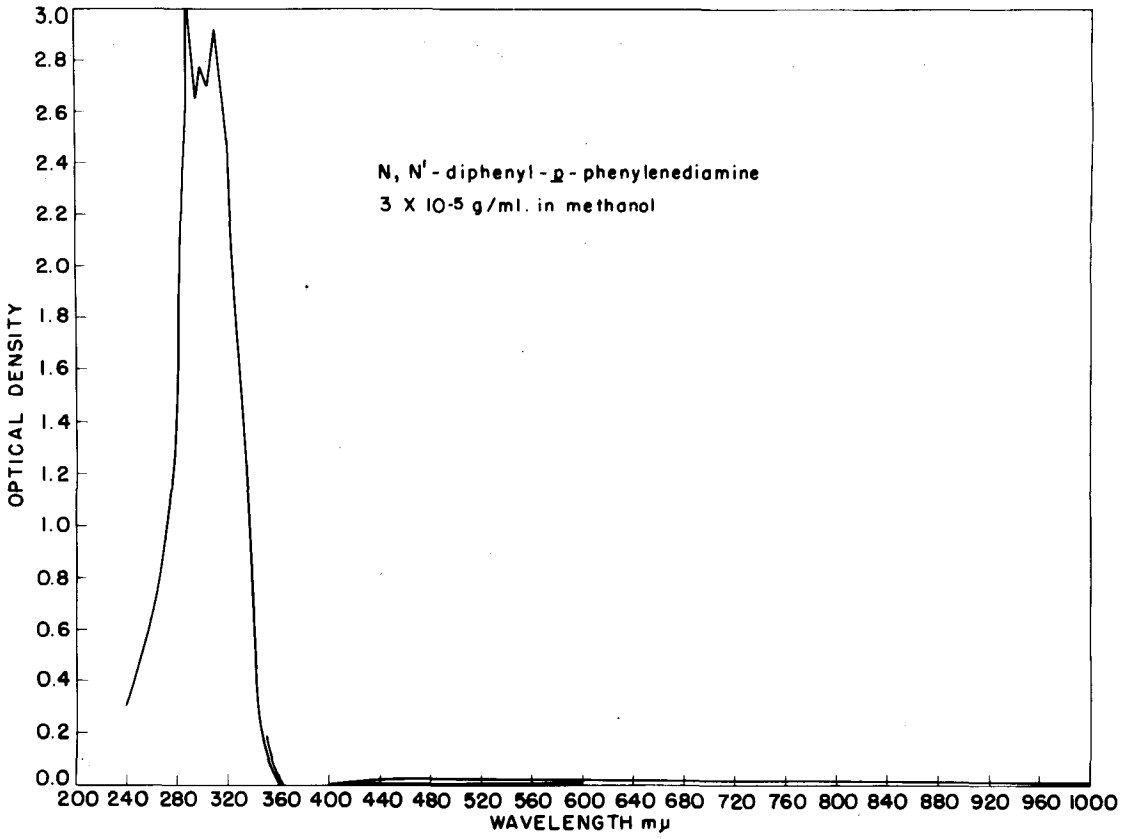
.00002436 g./ml. of quinhydrone,

.0000180 g./ml. of N,N'-diphenyl-p-phenylenediimine.

The spectra in the ultraviolet and visible were observed with a Beckman Model DU spectrophotometer. Sharp maxima were observed at 290 and 310 mμ for N,N'-diphenyl-p-phenylenediamine (see Fig. 1). Minima were at 295 and 380 mμ. For the quinhydrone (Fig. 2) there was a sharp maximum at 300 mμ and a low broad one at 440 mμ. A minimum was at 370 mμ. Since the first peak is nearly in the same position as for the pure amine, the optical density of this peak gives the total concentration of the quinhydrone base while the optical density at 440 mμ, which is due to dissociated N,N'-diphenyl-p-phenylenediimine (Fig. 3), is not as large as it should be (see Table 3), indicating that the quinhydrone is not completely dissociated in the solution. The maxima for the N,N'-diphenyl-p-phenylenediimine was at

Fig. 1 Ultraviolet and visible spectrum of N,N'-diphenyl-p-phenylene-diamine in methanol

Fig. 2 Ultraviolet and visible spectrum of the quinhydrone of N,N'-diphenyl-p-phenylenediamine in methanol


N, N'-diphenyl-p-phenylenediamine
3 X 10-5 g/ml. in methanol
OPTICAL DENSITY
WAVELENGTH mμ

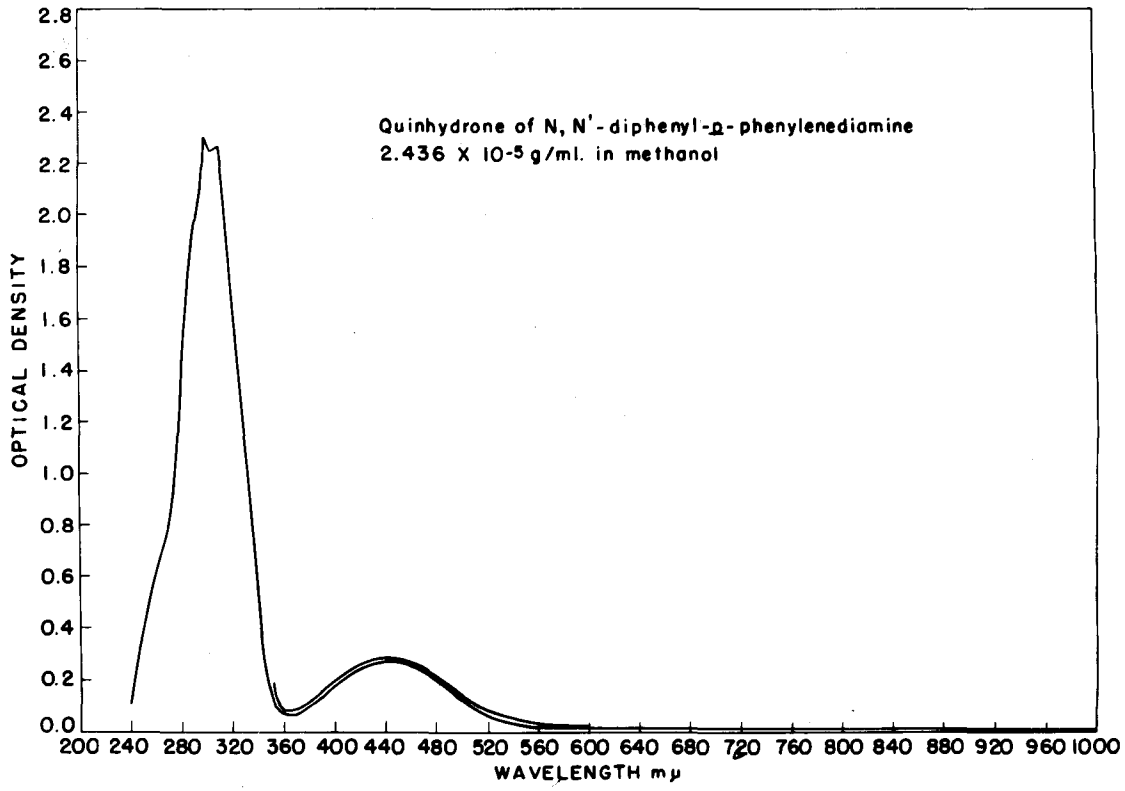
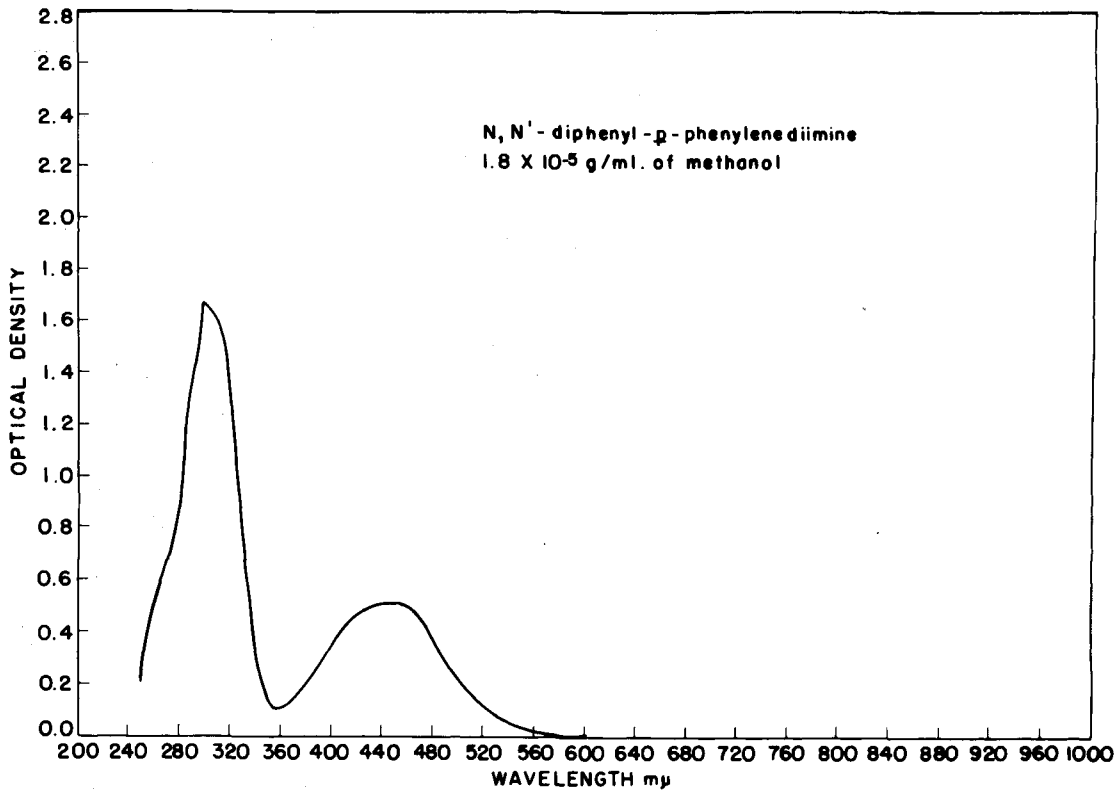

Quinhydrone of N, N'-diphenyl-p-phenylenediamine
2.436 X 10-5 g/ml. in methanol
OPTICAL DENSITY
WAVELENGTH mμ

Fig. 3 Ultraviolet and visible spectrum of N,N'-diphenyl-p-phenylene-diimine in methanol

Fig. 4 Ultraviolet and visible spectrum of oxidized N,N'-diphenyl-p-phenylenediamine in chlorobenzene and tetralin solution


N, N'-diphenyl-p-phenylenediimine
1.8 X 10-5 g/ml. of methanol
OPTICAL DENSITY
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
200 240 280 320 360 400 440 480 520 560 600 640 680 720 760 800 840 880 920 960 1000
WAVELENGTH mμ

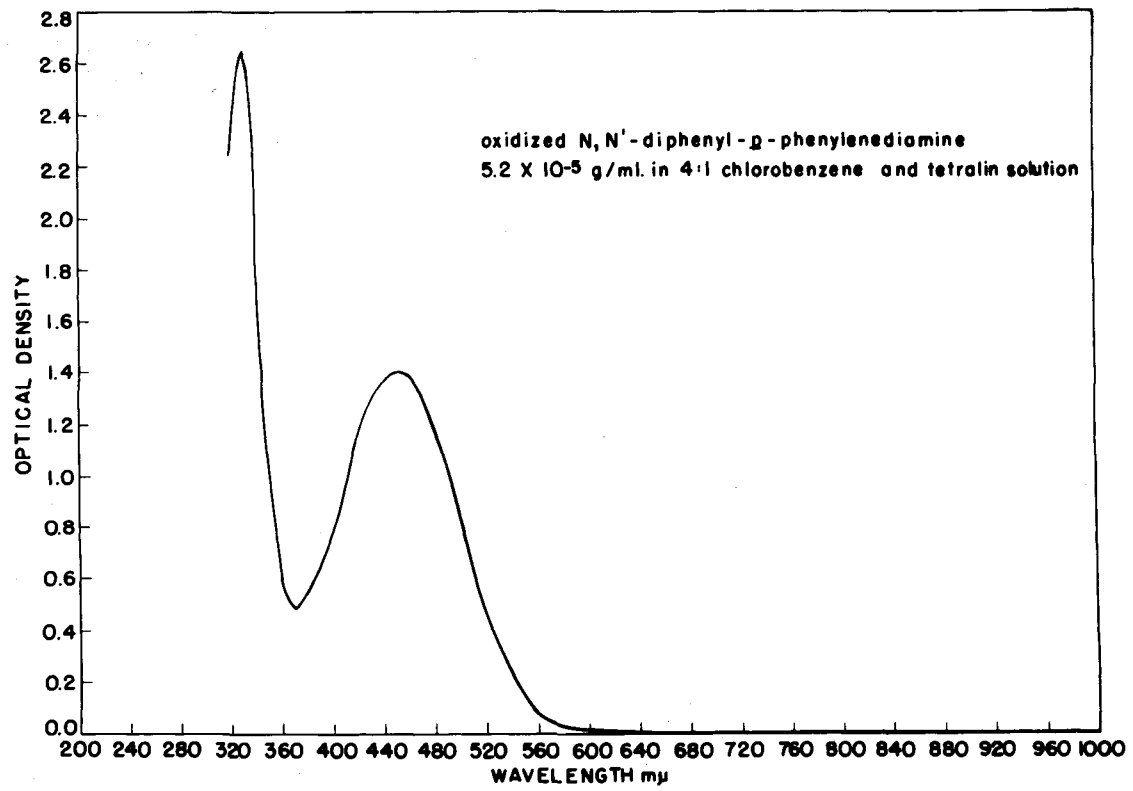

oxidized N, N'-diphenyl-p-phenylenediamine
5.2 X 10-5 g/ml. in 4:1 chlorobenzene and tetralin solution
OPTICAL DENSITY
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
200 240 280 320 360 400 440 480 520 560 600 640 680 720 760 800 840 880 920 960 1000
WAVELENGTH mμ

Table 3

Optical density from the spectrum of a known quantity of N,N'-diphenyl-p-phenylenediimine and quinhydrone in methanol

	Optical density	Concentration	
		Actual	Calculated
N,N'-diphenyl-p-phenylenediimine			
First peak (300 mμ)	1.66	1.8×10^{-5} g./ml.	-----
Second peak (440 mμ)	.51	1.8×10^{-5} g./ml.	-----
Quinhydrone			
First peak (300 mμ)	2.33	2.436×10^{-5} g./ml.	2.525×10^{-5} g./ml.
Second peak (440 mμ)	.27	1.218×10^{-5} g./ml.	$.952 \times 10^{-5}$ g./ml.

305 mμ and 440 mμ, the latter a broad flat maximum (see Fig. 3). The minimum is at 360 mμ.

Oxidation of N,N'-diphenyl-p-phenylenediamine in the kinetics apparatus and comparison of the spectrum with that of N,N'-diphenyl-p-phenylenediimine. A mixture of two ml. of chlorobenzene, one ml. of tetralin, two ml. of azo-bis-isobutyronitrile solution (.5004 g./10 ml. or 100 mg. of initiator) and two ml. of the inhibitor (.13 g./10 ml. or .0026 g. (10^{-5} moles) total inhibitor) [MW 260.33 g.] was placed in the reaction vessel. The rate was observed until the inhibition period was over and then the solution was taken from the reaction vessel. The reaction mixture was diluted by ten times with a 4:1 mixture of chlorobenzene and tetralin, making a solution of 2×10^{-7} moles per ml. = .000052 g. per ml. When comparing the spectrum of N,N'-diphenyl-p-phenylenediimine in

methanol (Fig. 3) and that of the oxidation products in tetralin and chlorobenzene (Fig. 4), optical density reading on the first peak on the lower wave lengths does not give reliable results in determining the concentrations of solute in solution since the maximum shifts from 300 mμ to 325 mμ. The lower, broader peak at 440 mμ gives more reliable results (see Table 3). Comparing the spectra of N,N'-diphenyl-p-phenylenediimine (Fig. 3) and its quinhydrone base (Fig. 2) which was obtained in the same solvent (methanol), results are more consistent (see Table 3). Since N,N'-diphenyl-p-phenylenediimine (Fig. 3) and N,N'-diphenyl-p-phenylenediamine (Fig. 1) both have maxima at 300 mμ, if the quinhydrone were completely dissociated the concentration for the second peak (440 mμ), which does not appear in the spectra of the unoxidized amine (Fig. 1), should be half that obtained at the first peak (300 mμ). The first peak gives concentrations very close to that of the quinhydrone base actually present (Fig. 2), while the results on the lower peak are 22 percent lower than the concentration of the N,N'-diphenyl-p-phenylenediimine present in the quinhydrone (compare Fig. 2 with Fig. 3), indicating that part of the oxidized form is complexed as the quinhydrone even at these dilutions (see Table 3). These results are consistent with what one might expect.

The calculations in Table 4 were obtained by using the optical density obtained for the quinoneimine in methanol (Fig. 3) to calculate the concentrations of this substance formed by air oxidation of N,N'-diphenyl-p-phenylenediamine in the presence of initiator radicals (Fig. 4). As mentioned previously, the shifted peak does not give reliable results. However, the second peak gives results very close to the theoretical amount possible if only quinoneimine were formed in the reaction.

Table 4

N,N'-diphenyl-p-phenylenediamine oxidized in tetralin and chlorobenzene

	Optical density	Concentration: Actual if 100% quinoneimine formed	Concentration: Calculated
First peak (325 mμ)	2.65	5.2×10^{-5} g./ml.	2.855×10^{-5} g./ml.
Second peak (440 mμ)	1.41	5.2×10^{-5} g./ml.	4.97×10^{-5} g./ml.

Separation and identification of products from the air oxidations of p,p'-dihydroxyazobenzene

First oxidation run. A mixture of 2.05 g. (.00957 mole) of p,p'-dihydroxyazobenzene, 3.75 g. (.02467 mole) of azo-bis-isobutyronitrile and 200 ml. of chlorobenzene were placed in a round bottom, three-necked flask equipped as described in the section on apparatus and procedures. The material did not dissolve at room temperature so it was placed in the water bath at 62.2°. After dissolution had appeared to take place, air was slowly bubbled through the solution. The color changed a light brown to a dark brown color. This color remained until the mixture was taken from the bath after 8 half lives for the initiator had passed (96 hours). The reaction mixture was decanted from the flask. About one g. of a dark residue was left in the flask. The dark colored solution was refrigerated overnight and filtered the next morning. A red-brown solid and a red solution were obtained. After removing most of the chlorobenzene by distillation at 50 mm. and 40°, the remainder was removed by evaporation. A dark colored solid material weighing 4.85 g. was recovered. The dark material,

which was obtained by decanting the original reaction mixture, proved to be interesting. The small, dark lumps proved to have a light brown center. The melting point of the dark outer material was 185-190°. The quinhydroneazine melts at 185°.[484] Inside the larger particles were found light brown, unreacted p,p'-dihydroxyazobenzene as indicated by the m.p. of 212-220°. The brown material changes to bright red on heating, as does the original starting material. This would indicate that among the products formed was the quinoneazine which formed a molecular complex with the unreacted starting material.

The solid material filtered from the cooled reaction mixture and the residue after removal of chlorobenzene both gave a white solid covered with small spherical deposits of orange-red oil on extraction with Skelly A and methylene chloride. This material was assumed to be tetramethylsuccinonitrile, but was never purified and identified. The residue from one (the material filtered from the original reaction mixture and then extracted with solvent) was a brown solid with some orange material. The residue from the other (the material from the chlorobenzene solution) was dark orange or reddish-brown oil. Numerous solvent extractions and recrystallizations were attempted, but no other product was isolated and identified.

Second oxidation run. A sample of finely divided p,p'-dihydroxyazobenzene was weighed out [1.538 g. (.00718 mole)] and placed in 200 ml. of chlorobenzene which was heated to boiling to try to dissolve the material. Not all of the material dissolved, but the residue appeared to be a fine powder so the run was continued. After the temperature had dropped to 50°, 2.813 g. (.0185 mole) of azo-bis-isobutyronitrile was added. The three-necked flask with the mixture was placed in the constant temperature bath

at 62.2°. Air was to be bubbled through as in the first oxidation. By mistake, suction was applied to the bubbler and part of the solution was lost. The run was continued, however, even when it was noted that some water had collected in the flask from the condenser due to the high humidity. At the end of 100 hours the run was stopped. There was quite a bit of solid material in the flask. This was filtered off and the solution was refrigerated. The solid material weighed 1.03 g. and consisted of a mixture of black and brown particles. Some of the black particles were picked out and were found to have a small amount of brown material in the center as in the previous run. The m.p. of the black material was 185-187°, which corresponds to the m.p. of the quinhydroneazine. The brown material of the mixture was not unreacted starting material, but behaved on the melting point block as did the pure quinoneazine. No melting point was observed even on heating to 310°. Assuming the solid to be mostly reaction products from the inhibitor, the amount unaccounted for is only .508 g. or .00217 mole. Part of this probably was lost at the beginning of the run.

The reaction mixture filtrate volume was 139 ml. By freezing in an acetone-dry ice mixture, a small amount of material was obtained which gave a peroxide test. It was a light yellow oil which turned red on standing in air. The filtrate was refrigerated for three weeks and then titrated for peroxide. A value of .00193 mole was obtained for the solution. By coincidence, this is close to the value of unaccounted-for inhibitor. However, this probably included peroxides from the initiator as well. The filtrate was extracted with 25 percent aqueous sodium hydroxide. After neutralization, neither fraction gave a test for peroxide. No further work was done with this mixture.

Spectrum of p,p'-dihydroxyazobenzene in methanol. The solution was .0000204 g. per ml. of p,p'-dihydroxyazobenzene. The spectrum (see Fig. 5) in the ultraviolet and visible was followed on a Beckman Model DU spectrophotometer. Sharp maxima were obtained at 246 mμ and 360 mμ. A minimum was observed at 270 mμ.

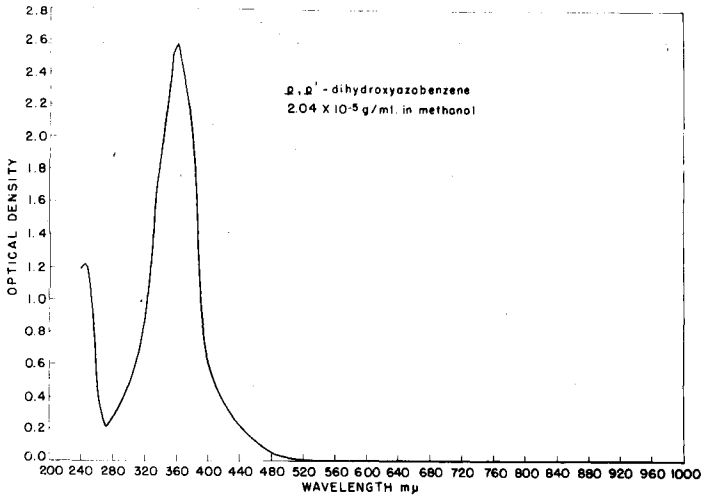
Spectrum of N,N'-diphenylquinonazine in tetralin and chlorobenzene. The solution was 2.118×10^{-5} g. per ml. of quinoneazine in four parts of chlorobenzene and one part tetralin. Maxima were at 335 mμ and 380 mμ and a minimum was observed at 370 mμ (see Fig. 6).

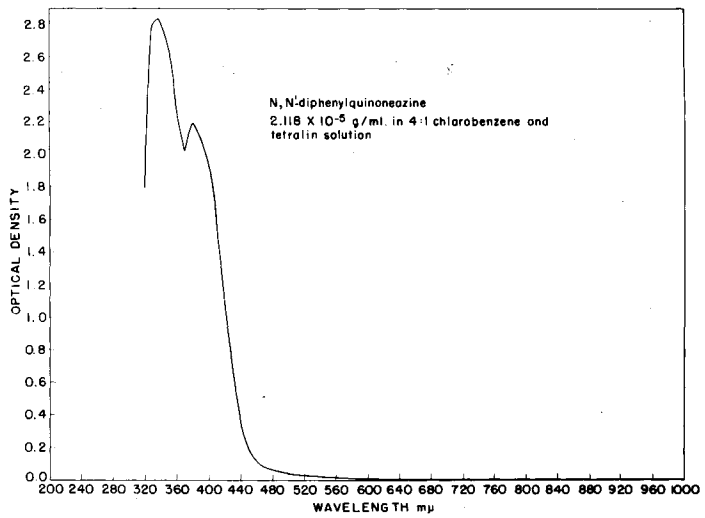
Oxidation of p,p'-dihydroxyazobenzene in the kinetics apparatus and the spectrum of the reaction mixture compared to that of N,N'-diphenylquinoneazine. A mixture of two ml. of chlorobenzene, one ml. of tetralin, two ml. of azo-bis-isobutyronitrile solution (.5004 g./10 ml. or 100 mg. total) and two ml. of inhibitor slurry (.107 g./10 ml. or 10^{-5} moles total inhibitor [MW 214.22 g.]) was placed in the reaction vessel. The rate was observed until the inhibition period was over, then the solution was taken from the reaction vessel. The mixture was diluted to ten times the volume by a mixture in the ratio of four ml. of chlorobenzene to one ml. of tetralin. The concentration of the oxidized inhibitor thus became 2×10^{-7} moles = .0000428 g. per ml. The ultraviolet and visible spectra were obtained (see Fig. 7). They corresponded to the spectrum of the known quinoneazine (Fig. 6), except there was a slight shift of the maxima to 345 mμ and 390 mμ with a minimum at 385 mμ. The conversion of p,p'-dihydroxyazobenzene to quinoneazine occurs in about 50 percent yield under the conditions of a kinetic run since the optical

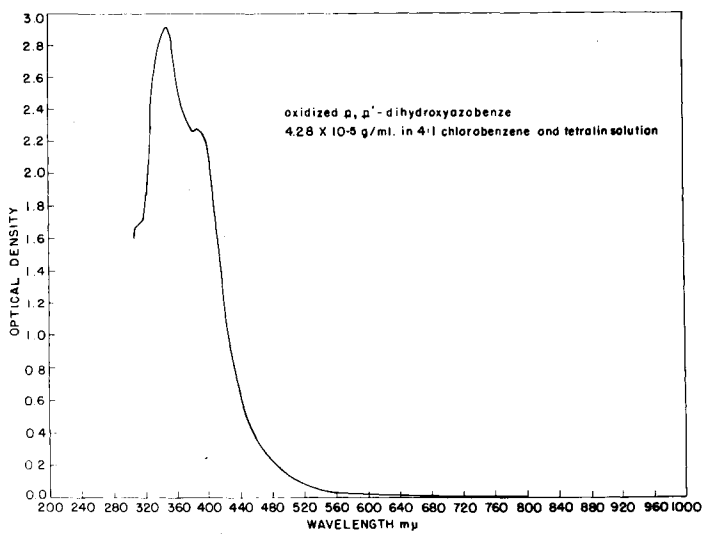
Fig. 5 Ultraviolet and visible spectrum of p,p'-dihydroxyazobenzene in methanol

Fig. 6 Ultraviolet and visible spectrum of N,N'-diphenylquinoneazine in chlorobenzene and tetralin solution

Fig. 7 Ultraviolet and visible spectrum of oxidized p,p'-dihydroxyazobenzene in chlorobenzene and tetralin solution


p,p'-dihydroxyazobenzene
2.04 X 10-5 g/ml. in methanol
OPTICAL DENSITY
WAVELENGTH mμ


N,N'-diphenylquinoneazine
2.118 X 10-5 g/ml. in 4:1 chlorobenzene and tetralin solution
OPTICAL DENSITY
WAVELENGTH mμ


oxidized p,p'-dihydroxyazobenze
4.28 X 10-5 g/ml. in 4:1 chlorobenzene and tetralin solution
OPTICAL DENSITY
WAVELENGTH mμ

density is approximately the same for the two spectra, yet the concentration of inhibitor in the oxidation run is twice that of the known sample of quinoneazine (see Tables 5 and 6).

Attempted preparation of diphenylperoxide by the air oxidation of phenylazotriphenylmethane

First oxidation run (at 25°). A mixture of 100 ml. of benzene and 17.4 g. (.05 mole) of phenylazotriphenylmethane was placed in a round bottom, three-necked flask and air was bubbled through the solution as described in the section on apparatus and procedures. The half life was calculated as 47 hours[581b] at 25° and it was decided to run the reaction for 5 half lives. A white precipitate was observed on dissolving the compound and was probably hydrazo contaminant. It soon dissolved. Soon a white precipitate appeared. During the run the benzene had to be replenished several times and the flask went dry several times overnight. At the end of the run the flask was dry, so the residue was extracted with Skelly B and the extract was chromatographed on alumina. A number of fractions gave a peroxide test, but most of these were solids. The residue which remained after filtering off the benzene reaction mixture weighed 4.62 g. and melted at 181-184°, indicating that it was ditritylperoxide. One of the better fractions from the column was recrystallized. The oily material in it was found to give a peroxide test while the solid did not. After considerable recrystallization from dry ice and acetone, an infrared spectra of the material was taken. An OH frequency was observed so the material was dissolved in Skelly A and placed over solid sodium hydroxide. A white finely divided material was filtered off and the Skelly A was

Table 5

Optical density from the spectrum of a known quantity of quinoneazine in methanol

	Optical density	Concentration Actual
First peak (335 mμ)	2.84	2.118×10^{-5} g./ml.
Second peak (380 mμ)	2.39	2.118×10^{-5} g./ml.

Table 6

p,p'-Dihydroxyazobenzene oxidized in tetralin and chlorobenzene

	Optical density	Concentration Actual	Theoretically possible
First peak (335 mμ)	2.9	2.15×10^{-5} g./ml.	4.28×10^{-5} g./ml.
Second peak (380 mμ)	2.27	2.02×10^{-5} g./ml.	4.28×10^{-5} g./ml.

evaporated off. Another infrared spectrum was taken. The OH frequency was gone. A white crystalline substance began to precipitate which gave a negligible peroxide test. The oil was not as good as that obtained in the next run, so work was concentrated on that run.

Second oxidation run (at 62.3°). The procedure was the same as in the first run, except that through a miscalculation the run went for 45 half lives (12.6 minutes at 62.3°). The white solid filtered out of the reaction mixture weighed 3.68 g. and melted at 184-186°, indicating that it was ditritylperoxide. The solution was titrated giving a total of .05557 mole

of peroxide in the solution. The benzene solution was distilled at reduced pressure and the oily residue extracted with n-pentane, followed by Skelly A and B, methylene chloride, acetone, ether and hot benzene. The material in n-pentane and the Skelly solvents was a light yellow oil. All the other residues proved to be ditritylperoxide. The oily material from the n-pentane and Skelly solvents was placed on the alumina column and chromatographed. The weight of material was about 6.75 g. The second fraction gave a good peroxide test so it was recrystallized repeatedly from a freezing mixture of dry ice and acetone. Infrared spectra indicated O-H present, so solid sodium hydroxide was used to precipitate the hydroperoxide from the Skelly B solution of the material. The infrared spectrum indicated that all hydroperoxide had been removed. A white crystalline substance began to precipitate slowly. This gave a negligible peroxide test. The oil gave a strong test which, however, developed slowly. However, after more crystallizations, the oil gave no more than 25 percent of the theoretical peroxide titer for diphenylperoxide.

Third oxidation run (at 62.2°). The oxidation was carried out as before for 2 hours (10 half lives). Most of the benzene was gone by the end of the run. The viscous yellow oil was extracted with pentane, which caused the separation of a white precipitate. The Skelly B solution of the oil was placed over sodium hydroxide for three days. After removal of hydroperoxide the material was chromatographed. None of the fractions gave a good test for peroxide. The solid residue obtained on extraction of the original reaction mixture weighed 9.28 g. and the m.p. was 109-113°. Since this material does not correspond to the m.p. of ditritylperoxide, which

should be produced in the reaction, it was assumed that lack of oxygen caused the production of the low melting material, so the run was discarded.

Fourth oxidation run (at 62.2°). A fourth run was started and handled much as before. No product was obtained.

DISCUSSION

A study of the mechanism of the air oxidation of unsaturated compounds in the presence of inhibitors was recently instituted in these laboratories. A typical oxidizable hydrocarbon, tetralin, was chosen for a standard substrate since its oxidation has been studied and the rate of decomposition of the derived peroxide is known. The thermal decomposition of azo-bis-isobutyronitrile in the presence of oxygen was used as a chain initiator for the oxidation reaction. The decomposition of the initiator is not sensitive to the presence of radicals.[589] The generally accepted mechanism of initiated air oxidation is the following:[72]

(1) $(CH_3)_2\overset{CN}{C}-N=N-\overset{CN}{C}-(CH_3)_2 \xrightarrow{k_d} 2\ (CH_3)_2\dot{C}CN + N_2$

(2) $(CH_3)_2\dot{C}CN + O_2 \xrightarrow{k_1} (CH_3)_2\overset{CN}{C}O_2\cdot$

(3) $CH_3\overset{CN}{C}O_2\cdot + RH \xrightarrow{k_2} (CH_3)_2\overset{CN}{C}O_2H + R\cdot$

(4) $R\cdot + O_2 \xrightarrow{k_3} RO_2\cdot$

(5) $RO_2\cdot + RH \xrightarrow{k_4} RO_2H + R\cdot$

(6) $2\ RO_2\cdot \xrightarrow{k_t}$ unknown products.

It cannot be assumed that the rate of initiation is equal to twice the rate of decomposition. Therefore, rate of initiation equals rate at which (2) occurs or

(7) $k_1 [(CH_3)_2\dot{C}CN][O_2] = 2\,ak_d[AIBN]$

where a is a factor which is one or less than one. By making the steady state approximation the rate law required by the above mechanism can be derived as follows:

(8) $\frac{d[R'\cdot]}{dt} = 2\,ak_d[I] - k_1[O_2]R' = 0$

$[I]$ is initiator concentration.

$[R'\cdot]$ is $(CH_3)_2\dot{C}CN$ concentration.

(9) $\frac{d[RO_2\cdot]}{dt} = k_1[O_2][R'\cdot] - k_2[RH][RO_2'] + k_3[R\cdot][O_2] - k_4[RO_2'][RH]$

$- 2\,k_t[RO_2\cdot]^2 = 0$

(10) $\frac{d[R\cdot]}{dt} = k_2[RH][RO_2'] - k_3[R\cdot][O_2] + k_4[RH][RO_2\cdot] = 0$

If one assumes $R'O_2\cdot$ and $RO_2\cdot$ have equal reactivities, then $k_2 = k_4$. This is probably approximately true. Then the following is true.

(11) $[R'\cdot] = \frac{2\,ak_d[I]}{k_1[O_2]}$

(12) $[RO_2\cdot] = \frac{ak_d[I]}{k_t}^{\frac{1}{2}}$

(13) $[R\cdot] = \frac{k_2[RH]\,(ak_dI)^{\frac{1}{2}}}{k_3[O_2]k_t^{\frac{1}{2}}}$

$$(14)\quad -\frac{d[O_2]}{dt} = k_1[R\cdot][O_2] + k_3[O_2][R\cdot]$$

$$(15)\quad -\frac{d[O_2]}{dt} = 2ak_d[I] + \frac{k_2[RH](ak_d[I])^{\frac{1}{2}}}{k_t^{\frac{1}{2}}}$$

This proposed mechanism then requires that the rate of the reaction shows (1) no dependence upon oxygen pressure, (2) half order dependence of the rate on initiator concentration, and (3) first order dependence of the rate on the concentration of the substrate (RH). If one assumes the other chain termination steps $2R\cdot \longrightarrow R_2$ or $R\cdot + RO_2\cdot \longrightarrow RO_2R$ as being in effect, then the rate becomes dependent on oxygen pressure. It was demonstrated that the three conditions demanded by the proposed mechanism were met by the systems studied.[136] In the presence of a good inhibitor the chain terminating step (equation 6) would be replaced by (16).

$$(16)\quad In + nRO_2\cdot \longrightarrow \text{products.}$$

This equation may possibly represent several steps for some inhibitors, however, several possibilities that suggest themselves, which would lead to different values for the stoichiometric factor n, are as follows:

(1) In the case that In is a free radical and adds to $RO_2\cdot$ n should equal one.

(2) If the reaction of In with $RO_2\cdot$ gave stable free radicals which destroyed each other by dimerization or other reactions n should equal one.

(3) If the inhibitor reacted with two $RO_2\cdot$ to give products which are stable in the presence of the other constituents of the reaction

mixture the n value would be two.

(4) If the products produced by the reaction of two $RO_2\cdot$ with In are unstable and react with more In to give stable products, n would equal one if a 1:1 ratio of product and inhibitor reacted.

(5) If the primary reaction of $RO_2\cdot$ with inhibitor gave a product which was itself an inhibitor, then higher n values would result, which vary according to the nature of the succeeding reactions.

In order to determine the stoichiometric factor n, two methods of approach are applicable. If one accurately determines the rate of initiation of the reaction, then measures with a like accuracy the lifetime of an inhibitor which is present in known concentration, one may calculate the number of chains ($RO_2\cdot$) which each inhibitor has stopped. This is relatively simple and a very good method for those inhibitors with well defined inhibition periods. The difficulty in the method lies in determining the efficiency of chain initiation which is obtained when an initiator undergoes thermal decomposition. Most of the commonly used initiators do not give a quantitative yield of two chain initiating radicals per molecule when they undergo decomposition as implied by equation (1).[420,421] Therefore, the rate of initiation of chains is some fractional value of twice the decomposition rate (equation 7). From equation (15), it would appear that by measuring the rate of nitrogen evolution from the initiator in the absence of oxygen and then by measuring the rate of uptake of oxygen by the initiator as it decomposed thermally in the presence of oxygen, one could determine the efficiency factor (a). However, this did not prove to be the case, probably due to the production of unstable products, since approximately as much oxygen was used as there was nitrogen released.[420] This

would give an efficiency factor of one which does not correlate with other facts obtained by trapping the chain initiating radicals with various scavengers such as mercaptans, iodine and inhibitors,[421] all of which correlate well with each other.

Another independent method of determining the stoichiometry of the reaction of peroxy radicals with an inhibitor is that of product analysis. If one carries out a careful study of the products from the inhibition reaction, one may infer from the products the number of chains which the inhibitor has terminated. An important feature of the product study is the necessity of obtaining practically a quantitative recovery, along with the separation and identification of products. Small amounts of a substance isolated from a reaction mixture in small yield is no guarantee that one will be able to infer the principle course of the reaction from it. Although a thorough product study is slow and time consuming, the information gained from it can be very useful and can help a great deal in determining the stoichiometry of the inhibitor in question, and may be applied to others as well. Since one successful product analysis and assignment of stoichiometry is also a measure of initiator efficiency, the lifetime method previously mentioned may be used to determine the stoichiometry of other inhibitors under the same reaction conditions. It is also possible to check assignments of stoichiometry for various inhibitors for reasonableness and consistency by comparing the results obtained with the various inhibitors.

The attack reported in this thesis upon the problem of the stoichiometry of the reaction of peroxy radicals with inhibitors is based upon product identification. To be successful the method requires:

(1) Quantitative material balance.

(2) The products isolated must be related to a particular stoichiometry of reaction of $RO_2\cdot$ with inhibitor in a reasonable manner.

The inhibitor first chosen for study was diphenylamine, which has long been known as an antioxidant. The substrate chosen was tetralin, a compound whose air oxidation has been extensively studied. The initiator chosen was azo-bis-isobutyronitrile, a well-known initiator whose decomposition rate is not sensitive to the presence of radicals as previously mentioned.[589] A great deal of time was spent in trying to obtain products from the air oxidation of diphenylamine inhibited systems without success. The only products separated and identified were tetralin, diphenylamine and tetramethylsuccinonitrile, a coupling product of the radicals produced by the decomposition of azo-bis-isobutyronitrile. By this time, kinetic evidence was sufficient to establish the fact that diphenylamine exhibited a nonintegral stoichiometry with respect to reaction with peroxy radicals, whereas, most other good inhibitors exhibit a stoichiometry of two.[136] For this reason further work with diphenylamine was not undertaken. During this part of the investigation, however, a fact was established which coincided with the results of the work of Hammond, Sen and Boozer[421] concerning the efficiency of radical production from azo-bis-isobutyronitrile. By means of radical traps (butylmercaptan, iodine and oxygen) it was established that only 60 percent of the radicals produced in chlorobenzene solution could be trapped. (The efficiency varies with the solvent.) The remainder formed the dimer which was produced after release of nitrogen from the initiator with formation of radicals and before the radicals could diffuse away from each other in the solvent and react with the trapping

compounds. In one of the experiments in which the oxidation of the diphenylamine was initiated by peroxy radicals produced from oxygen reacting with the available radicals from the thermal decomposition of azo-bis-isobutyronitrile, there was recovered 44 percent of the total charge of initiator in the form of tetramethylsuccinonitrile. This indicates that the efficiency of radical production was 56 percent and agrees well with the 60 percent obtained by kinetic measurements. The difference may be due to poorer distribution of oxygen in the large scale run. As previously mentioned, a knowledge of the efficiency of peroxy radical production is necessary in establishing the stoichiometry of reaction of peroxy radicals with inhibitors by the lifetime of inhibitor method. For this reason, the above independent confirmation by obtaining the actual product formed by the radicals which did not initiate chains is of importance in establishing the mechanism of reaction. The isolation of the dinitrile is semiquantitative confirmation of the efficiency factor ultimately assigned.

Another inhibitor chosen for study was N,N'-diphenyl-p-phenylenediamine. From a large scale oxidation reaction a 46 percent yield of N,N'-diphenylquinonediimine was isolated from the reaction mixture, with properties which identified it as the same as the compound prepared by independent synthesis. With this excellent yield, it was decided to obtain the ultraviolet spectrum of a known sample of N,N'-diphenylquinonediimine and compare it with the spectrum of the reaction mixture obtained under the conditions used in the kinetics apparatus when N,N'-diphenyl-p-phenylenediamine was used as the inhibitor. It was thus established that 90-96 percent of the inhibitor was converted to the product previously isolated. With this excellent yield, the course of the reaction must certainly be

(17) $2\ RO_2\cdot + ArN\text{-}C_6H_4\text{-}NAr \longrightarrow 2\ RO_2H + ArN{=}C_6H_4{=}NAr$

since the need of two $RO_2\cdot$ to abstract the hydrogen is quite apparent. In this way, the stoichiometric factor was assigned and the efficiency of radical initation determined, which agreed with the results previously obtained in the work on diphenylamine and with other workers in the laboratory.[136]

It has commonly been assumed that the rate determining step in the reaction of peroxy radicals with inhibitors is the abstraction of hydrogen from the inhibitor. However, kinetic isotope studies did not bear this out.[420] On the basis of the termolecular order of the reaction and the lack of kinetic isotope effect, it was proposed that reversible complexing first took place between a peroxy radical and the inhibitor followed by the attack of the second peroxy radical.

(18) $$RO_2\cdot + In \underset{}{\overset{K_c}{\rightleftharpoons}} \overline{RO_2\cdot} \longrightarrow \overline{In}$$

(19) $$\overline{RO_2\cdot} \longrightarrow \overline{In} + RO_2\cdot \xrightarrow{k_{In'}} \text{products.}$$

If only a small part of the $RO_2\cdot$ radicals are complexed, and the following reaction is very rapid, no isotope effect would be observed. Thus dehydrogenation can be the overall change despite the indication that abstraction is not the first step.

Another assumption which has often been made is that a good inhibitor must have a labile hydrogen, since it was assumed ease of hydrogen removal was important in the rate determining step. However, a case of a good

inhibitor has recently been reported[135] which had no labile hydrogen and other cases have been reported in which products were obtained in which one peroxy radical abstracted hydrogen and the second gave substitution on the benzene ring.[110b,136,704] However, it might still be assumed that a compound with two labile hydrogens would be expected to lose them quite easily and thus form a dehydrogenated product exclusively. Such did not prove to be the case upon the oxidation of p,p'-dihydroxyazobenzene. The expected product, quinoneazine, was synthesized and its spectrum and the spectrum of oxidized p,p'-dihydroxyazobenzene were compared. In this case, only 50 percent of the starting material lost two hydrogens to form the quinoneazine. The identity of the other product is not known. In all probability a peroxy radical has been substituted at some position. In so doing, it must deactivate the rest of the molecule with respect to further reaction with peroxy radicals. This would be necessary or the stoichiometric factor would not be two, as determined by the lifetime method. The inactivation of the ring may come from the peroxy substituent preventing further complexing with peroxy radicals.

Kinetics demands that in the chain termination of uninhibited air oxidation of olefins two peroxy radicals destroy themselves or react with solvent and go to stable products (equation 6). With a tertiary R· this reaction is hard to formulate. Since $(CH_3)_2\dot{C}$-CN is a radical with a tertiary carbon it was felt that the study of the oxidation of the initiator might prove to be rewarding. Kinetic studies were made on the volume of gas consumed during the oxidation of initiator in order to determine if the following reactions were probable.

(20) $2\,(CH_3)\underset{CN}{C}O_2\cdot \longrightarrow (CH_3)_2\underset{CN}{C}-OO-\underset{CN}{C}(CH_3)_2 + O_2$

(21) $2\,(CH_3)_2\underset{CN}{C}O_2\cdot \longrightarrow (CH_3)_2CO_2H + CH_2=\underset{CH_3}{C}-CN + O_2$

Since the efficiency of initiation is only 0.65 in chlorobenzene it would be expected the total gas volume should expand from the N_2 released by the initiator if either reaction occurred. It was found that the oxygen uptake exceeds by a slight amount the rate of nitrogen evolution.[420] A large scale oxidation was carried out. It was noted that a very much lower peroxide content was obtained than was theoretically to be expected if the peroxides were stable. It was also noted that there was hydrogen cyanide gas in the vapors over the reaction mixture. These same results were noted in other runs in which inhibitors or other substrates were used, indicating that the $(CH_3)_2\underset{CN}{C}OOH$ which one might assume to be formed at least to some extent was not stable. Perhaps the decomposition of the peroxide derived from the initiator may have proceded along a path such as the following:

(22) $$CH_3-\overset{CH_3}{\underset{CN}{C}}-O-O-X \longrightarrow CH_3-\overset{CH_3}{\underset{CN}{C}}-O\cdot + XO\cdot$$

$$\downarrow\ ?$$

$$(CH_3)_2C=O + \cdot CN \xrightarrow{\ ?\ } HCN$$

An attempt was made to utilize air oxidation for the preparation of diphenylperoxide or phenylhydroperoxide. These represent a class of compounds which have not yet been prepared. It would be desirable to obtain them since they might have interesting properties. The diphenylperoxide

might be similar to hydrazobenzene and give the benzidine rearrangement. Also it would probably be a good source of the phenoxy radical, producing only one kind of radical in decomposition, and thus being of interest as a chain initiator.

It was hoped that the following reaction would take place in aromatic solvent:

(23) $\phi_3CN{=}N{-}\phi \longrightarrow \phi_3C\cdot + O\cdot + N_2$

(24) $\phi\cdot + O_2 \longrightarrow \phi O_2\cdot$

(25) $\phi O_2\cdot + ArH + R\cdot' \longrightarrow \phi O_2Ar + R'H$

If $R' = \phi O_2\cdot$ this gives ϕO_2H.

Results indicate that phenylperoxy compounds may have been produced. However, if they were formed they decomposed at low temperature with formation of $\phi O\cdot$ which underwent coupling or aromatic substitution reactions.

SUMMARY

1. The determination of the stoichiometry of the reaction of peroxy radicals with inhibitors was attacked by an analysis of reaction products. An attempt was made to obtain a quantitative material balance and, from the products isolated, establish the stoichiometry of reaction as well as the efficiency of initiation by the initiator of the reaction. This was accomplished. An excellent yield of the oxidation product of N,N'-diphenyl-p-phenylenediamine was obtained and through ultraviolet spectra it was determined that N,N'-diphenyl-p-phenylenediimine was obtained in 90-96 percent yield. From this, the stoichiometry was assigned as two and the efficiency of initiation was determined. Previous work leading to the isolation of tetramethylsuccinonitrile from radicals which did not start chains also was in agreement in assigning the efficiency of chain initiation. Other work with diphenylamine was without result.

2. It was shown that an inhibitor with labile hydrogen does not always lose hydrogen as a principle course of reaction when attacked by peroxy radicals. It was shown that p,p'-dihydroxyazobenzene gave the quinoneazine in only 50 percent yield.

3. Studies of termination reactions of the uninhibited air oxidation of olefins proved unlikely to be rewarding because of the instability of the primary products.

4. An attempt was made to utilize air oxidation as a means of preparing diphenylperoxide or phenylhydroperoxide. This proved unsuccessful.

BIBLIOGRAPHY

1. Ackerman and Moberly, U. S. Patent 2,573,294. Abst. in C. A. 46: 7579 (1952).
2. Adelson, U. S. Patent 2,512,784. Abst. in C. A. 44:8634 (1950).
3. _____, U. S. Patent 2,574,994. Abst. in C. A. 46:2289 (1952).
4. _____, U. S. Patent 2,576,895. Abst. in C. A. 46:9588 (1952).
5. _____, U. S. Patent 2,652,367. Abst. in C. A. 48:354 (1954).
6. Aktieselskabet Niro Atomizer, Dan. Patent 64,773. Abst. in C. A. 41:987 (1947).
7. Albert, Ind. Eng. Chem., 40, 1746-50 (1948).
8. _____, U. S. Patent 2,514,179. Abst. in C. A. 44:9720 (1950).
9. _____, U. S. Patent 2,514,188. Abst. in C. A. 44:9720 (1950).
10. _____, U. S. Patent 2,581,919. Abst. in C. A. 46:3791 (1952).
11. _____, U. S. Patent 2,581,930. Abst. in C. A. 46:4265 (1952).
12. _____, U. S. Patent 2,581,931. Abst. in C. A. 46:4266 (1952).
13. _____, U. S. Patent 2,605,249. Abst. in C. A. 46:10675 (1952).
14. _____, U. S. Patent 2,626,954. Abst. in C. A. 47:4121 (1953).
15. _____, U. S. Patent 2,632,754. Abst. in C. A. 47:7250 (1953).
16. Alekseenko, Zaionchkovskiĭ, Mishuatin and Guchkova, Legkaya Prom., 5, No. 5, 20-3 (1945).
17. Alexander, U. S. Patent 2,559,580. Abst. in C. A. 45:10547 (1951).
18. Allen, J. Inst. Petroleum, 31, 9-15 (1945).
19. _____ and Byers, U. S. Patent 2,345,439. Abst. in C. A. 45:7147 (1951).
20. Altman, Dutch Patent 67,611. Abst. in C. A. 45:10654 (1951).
21. _____ and van der Bie, Ind. Eng. Chem., 40, 897-904 (1948).
22. Alyea and Backstrom, J. Am. Chem. Soc., 51, 90 (1929).
23. Ambelang, U. S. Patent 2,647,102. Abst. in C. A. 47:10887 (1953).

24. Amberg, U. S. Patent 2,600,886. Abst. in C. A. 46:11755 (1952).

25. Am. Cyanamid Co., Brit. Patent 589,051. Abst. in C. A. 42:601 (1948).

26. Amott, U. S. Patent 2,397,332. Abst. in C. A. 40:3890 (1946).

27. Anderson, Betzold and Carr, Food Technol., 4, 297-300 (1950).

28. Angel, Fuller and Berger, U. S. Patent 2,381,377. Abst. in C. A. 40:1998 (1946).

29. Anglamol Ltd., Brit. Patent 654,968. Abst. in C. A. 46:3252 (1952).

30. _____, Brit. Patent 682,441-2. Abst. in C. A. 47:6647 (1953).

31. Antle and Bohn, U. S. Patent 2,628,905. Abst. in C. A. 47:4521 (1953).

32. Anzaldi, Rev. fac. cienc. quím. (Univ. nacl. La Plata), 23, 163-70 (1948).

33. Arditti, Groupement franc., develop. recherches aeronaut., Note tech. No. 10, 36 pp. (1943).

34. Arey and Wood, U. S. Patent 2,650,208. Abst. in C. A. 48:1050 (1954).

35. Armistead, Oil Gas J., 44, No. 49, 97-103 (1946).

36. Asano and Gisvold, J. Am. Pharm. Assoc., 38, 169-73 (1949).

37. Atkinson, Morgan, Warren and Manning, J. Am. Chem. Soc., 67, 1513 (1945).

38. Audrieth, U. S. Patent 2,374,969. Abst. in C. A. 39:5099 (1945).

39. _____ and Mohr, U. S. Patent 2,544,772. Abst. in C. A. 45:4470 (1951).

40. Augustine, U. S. Patent 2,528,732. Abst. in C. A. 45:3863 (1951).

41. Ault, Nutting and Weil, U. S. Patent 2,595,221. Abst. in C. A. 47: 1190 (1953).

42. Aure, Fiskeridirektoratets Skrifter, 1, No. 10, 3-15 (1951).

43. Babcock, Strobel, Yager and Windham, J. Dairy Sci., 35, 195-8 (1952).

44. Bacha, Rev. facultad. cienc. quím., 22, 255-7 (1947) (Pub. 1949).

45. Bacq, Fischer and Lecomte, Arch. intern. physiol., 56, 25-7 (1948).

46. _____, Lecomte and Fischer, Compt. rend. soc. biol., 142, 1068 (1948).

47. Badertscher, U. S. Patent 2,355,257. Abst. in C. A. 38:6548 (1944).

48. Bailey and Feuge, Oil & Soap, 21, 286-8 (1944).

49. _____, Oliver, Singleton and Fisher, Oil & Soap, 20, 251-5 (1943).

50. Baker, J. Appl. Chem. (London), 3, 323-8 (1953).

51. Baldinger, Ellis and Fawcett, J. Am. Pharm. Assoc., 33, 41-3 (1944).

52. Balsbaugh, ASTM Bull., 149, 7583 (1947).

53. Banerji and Mukherji, Indian Soap J., 13, 6-9 (1947).

54. Banks, J. Soc. Chem. Ind., 63, 873 (1944).

55. _____ and Lovern, Brit. Patent 552,809. Abst. in C. A. 38:4385 (1944).

56. Barac, Compt. rend. soc. biol., 145, 1900-3 (1951).

57. _____ and Roseman, Bull. soc. chim. biol., 28, 612-14 (1946).

58. _____ and _____, J. Wash. Acad. Sci., 36, 296-301 (1946).

59. Barnes, U. S. Patent 2,448,207. Abst. in C. A. 43:884 (1949).

60. Barthel, U. S. Patent 2,576,094. Abst. in C. A. 46:4814 (1952).

61. _____ and Hastings, U. S. Patent 2,680,694. Abst. in C. A. 48: 10357 (1954).

62. Bartleson, U. S. Patent 2,432,713. Abst. in C. A. 42:2131 (1948).

63. _____, U. S. Patent 2,476,271. Abst. in C. A. 43:8668 (1949).

64. _____, U. S. Patent 2,534,217. Abst. in C. A. 45:2194 (1951).

65. _____, U. S. Patent 2,584,977. Abst. in C. A. 46:4216 (1952).

66. _____ and Campbell, U. S. Patent 2,655,477. Abst. in C. A. 48: 994 (1954).

67. _____ and Hughes, U. S. Patent 2,542,981. Abst. in C. A. 45:4034 (1951).

68. _____ and Sunday, Ind. Eng. Chem., 41, 924-8 (1949).

69. Bartlett, U. S. Patent 2,656,318. Abst. in C. A. 48:1669 (1954).

70. _____ and Cross, U. S. Patent 2,631,130. Abst. in C. A. 47:5110 (1953).

71. Basinski and Tyrakowski, Roczniki Chem., 27, 102-15 (1953).

72. Bateman, Quarterly Revs., 8, 147 (1954).

73. _____ and Bolland, Proc. Itern. Congr. Pure & Applied Chem., 11, 325-32 (1947).

74. Basu and Bhattacharya, Indian Pharmacist, 5, 172-4 (1950).

75. _____ and _____, J. Indian Chem. Soc., 26, 459-66 (1949).

76. _____ and _____, J. Indian Chem. Soc., 27, 169-74 (1950).

77. _____ and _____, Science and Culture, 14, 481-2 (1949).

78. Bauernfeind, Batcher and Shaw, Glass Packer, 26, 268-9, 358-61 (1947).

79. _____, Smith and Siemers, Food Technol., 5, 254-60 (1951).

80. Baxter, Stern and Weisler, U. S. Patent 2,486,541. Abst. in C. A. 44:2038 (1950).

81. Bayes, U. S. Patent 2,364,122. Abst. in C. A. 39:3925 (1945).

82. _____, U. S. Patent 2,368,022-3. Abst. in C. A. 39:3925 (1945).

83. _____, U. S. Patent 2,384,002. Abst. in C. A. 40:732 (1946).

84. Beadle, Advances in Chemistry, Ser. 3, 55-60 (1950).

85. _____ and Kraybill, U. S. Patent 2,648,608. Abst. in C. A. 47: 11763 (1953).

86. Beare, Kleinholz and Hoock, U. S. Patent 2,619,462. Abst. in C. A. 47:2973 (1953).

87. Beau, Rev. gén. caoutchouc, 31, 49-53 (1954).

88. Beaver, U. S. Patent 2,364,338. Abst. in C. A. 39:4257 (1945).

89. _____, U. S. Patent 2,668,161. Abst. in C. A. 48:5542 (1954).

90. _____ and Magnon, U. S. Patent 2,670,383. Abst. in C. A. 48:7333 (1954).

91. Beegle, Brit. Patent 700,303. Abst. in C. A. 48:5485 (1954).

92. Beerbower and Darley, U. S. Patent 2,337,478. Abst. in C. A. 38: 3831 (1944).

93. Bell, U. S. Patent 2,531,602. Abst. in C. A. 45:3407 (1951).

94. _____ and Shields, U. S. Patent 2,639,288. Abst. in C. A. 47: 8394 (1953).

95. Benk, Seifen-Öle-Fette-Wachse, 75, 536-7 (1949).

96. Benmels, U. S. Patent 2,615,059. Abst. in C. A. 47:1970 (1953).

97. Bentz, Modern Packaging, 27, No. 1, 141-3 (1953).

98. _____, O'Grady and Wright, Food Technol., 6, 302-4 (1952).

99. Berberich, ASTM Bull., 149, 65-74 (1947).

100. Bergel, Chemistry & Industry, 14, 127-8 (1944).

101. Bergen, U. S. Patent 2,343,393. Abst. in C. A. 38:3831 (1944).

102. _____, U. S. Patent 2,385,964. Abst. in C. A. 40:5562 (1946).

103. Berger and Fuller, U. S. Patent 2,442,915. Abst. in C. A. 42:7522 (1948).

104. Berry, Pharm. J., 154, 94-6 (1945).

105. Bersworth, U. S. Patent 2,564,092. Abst. in C. A. 46:1030 (1952).

106. Berthollet, Journ. de l'Esle polytechn., Series 3, 277 (1797).

107. Bertram and Wynia, J. Am. Oil Chemists' Soc., 29, 629-31 (1952).

108. Better and Davidsohn, Oil & Soap, 23, 245-7, 283-4 (1946).

109. Bibby, Food Manuf., 20, 441-3, 448 (1945).

110a. Bickel, J. Chem. Soc., 3211 (1953).

110b. _____ and Koojman, J. Chem. Soc., 3211 (1953).

111. Bickford, Pack, Castillon and Mack, J. Am. Oil Chemists' Soc., 31, 91-3 (1954).

112. Bickoff, J. Am. Oil Chemists' Soc., 28, 65-8 (1951).

113. _____, Coppinger, Livingston and Campbell, J. Am. Oil Chemists' Soc., 29, 51-3 (1952).

114. _____, Livingston, Guggolz and Thompson, J. Am. Oil Chemists' Soc., 29, 445-6 (1952).

115. _____ and Williams, Oil & Soap, 23, 65-8 (1946).

116. _____, _____ and Sparks, Oil & Soap, 22, 128-31 (1945).

117. Bielstein, 7:Syst. No. 671, p. 628 (345).

118. Biswell, U. S. Patent 2,584,784. Abst. in C. A. 47:607 (1953).

119. Bittenbender, Com. Fisheries Rev., 12, No. 2, 1-18 (1950).

120. Bittles and Joyce, U. S. Patent 2,559,754. Abst. in C. A. 46:1026 (1952).

121a. Black, Can. Patent 431,986. Abst. in C. A. 40:2014 (1946).

121b. _____, U. S. Patent 2,408,904. Abst. in C. A. 41:1120 (1947).

122. Blaisten, Rev. asoc. bioquim. argentina, 14, 181-2 (1947).

123. Blaizot and Cuvier, Oleagineux, 5, 96-100 (1950).

124. Blake, U. S. Patent 2,469,101. Abst. in C. A. 43:5626 (1949).

125. _____, U. S. Patent 2,506,410. Abst. in C. A. 44:7087 (1950).

126. _____, U. S. Patent 2,544,292. Abst. in C. A. 45:5452 (1951).

127. Bloch, U. S. Patent 2,648,640. Abst. in C. A. 47:11758 (1953).

128. Boehm and Williams, Pharm. J., 151, 163-4 (1943).

129. _____ and _____, Quart. J. Pharm. Pharmacol., 16, 232-43 (1943).

130. _____ and _____, Quart. J. Pharm. Pharmacol., 17, 171-7 (1944).

131. Bogaty, Ann. Dyestuff Reptr., 38, 253-9 (1949).

132. Bolland, Proc. Ray. Soc., A, 186, 218 (1946).

133. _____ and Ten Have, Discussions Faraday Soc. 1947, No. 2, 252-60.

134. Bolomey, J. Biol. Chem., 169, 323-29 (1947).

135. Boozer and Hammond, J. Am. Chem. Soc., 76, 3861 (1954).

136. _____, _____, Hamilton and Sen. The stoichiometry and fate of inhibitors in benzene and chlorobenzene. [Unpublished research.] Iowa State College, Ames, Iowa. (1954).

137. Bose, Current Sci., 16, 119-20 (1947).

138. _____, Rao and Subrahmanyan, J. Sci. Ind. Research, 9B, 37-42 (1950).

139. _____ and Subrahmanyan, Indian J. Med. Research, 37, 11-18 (1949).

140. _____ and _____, J. Sci. Ind. Research, 9, 122-7 (1950).

141. Boutaric and Maraux, Ann. pharm. franc., 6, 347-50 (1948).

142. Boyd, U. S. Patent 2,507,755. Abst. in C. A. 44:8369 (1950).

143. _____ and Peterson, Ind. Eng. Chem., 37, 370-3 (1940).

144. Branthoover and Hard, Science, 114, 296-8 (1951).

145. Briggs and Blackley, U. S. Patent 2,559,932. Abst. in C. A. 45:9299 (1951).

146. _____ and Haworth, Brit. Patent 621,004. Abst. in C. A. 43:7257 (1949).

147. _____, _____ and Jackson, Brit. Patent 622,977. Abst. in C. A. 43:7257 (1949).

148. Brit. Resin Products Ltd., Brit. Patent 662,509. Abst. in C. A. 46: 7317 (1952).

149. Brock, Johnson and Armstrong, U. S. Patent 2,409,828. Abst. in C. A. 41:1250 (1947).

150. Broglia, Chimica, 5, 13-22 (1950).

151. _____, Mondo latte, 1949, 307-8, 311, 313-14.

152. Brooks, U. S. Patent 2,522,489-90. Abst. in C. A. 44:11083 (1950).

153. _____, U. S. Patent 2,540,093. Abst. in C. A. 45:4033 (1951).

154. _____, U. S. Patent 2,576,071. Abst. in C. A. 46:1244 (1952).

155. _____ and Sachanen, U. S. Patent 2,534,223. Abst. in C. A. 45: 2198 (1951).

156. Browder, U. S. Patent 2,638,412. Abst. in C. A. 47:6644 (1953).

157. Brown, U. S. Patent 2,377,610. Abst. in C. A. 39:3952 (1945).

158. Bucher, Fishery Market News, 7, No. 7, 17-19 (1945).

159. Buckwalter, U. S. Patent 2,650,891. Abst. in C. A. 48:1022 (1954).

160. Budowski, J. Am. Oil Chemists' Soc., 27, 264-7 (1950).

161. Buffa, Conserve e deriv. agrumari (Palermo), 1, No. 1, 10-12 (1952).

162. Buffington, U. S. Patent 2,442,341. Abst. in C. A. 42:5709 (1948).

163. Bunyatyan and Kamalyan, Biokhimiya, 15, 283-6 (1950).

164. Burk and Hughes, U. S. Patent 2,328,190. Abst. in C. A. 38:1104 (1944).

165. _____ and _____, U. S. Patent 2,367,264. Abst. in C. A. 39: 2869 (1945).

166. Burke, U. S. Patent 2,374,077. Abst. in C. A. 39:3694 (1945).

167. Burroughs, U. S. Patent 2,462,608-9. Abst. in C. A. 43:4511 (1949).

168. Burtner, U. S. Patent 2,590,086. Abst. in C. A. 46:10206 (1952).

169. Busch, Decker and Ashworth, J. Dairy Sci., 35, 524-32 (1952).

170. Bushland, Schechter, Jones and Knipling, Soap Sanit. Chemicals, 21, No. 11, 119, 121 (1945).

171. Buxton, Ind. Eng. Chem., 39, 225-32, 1171-4 (1947).

172. _____, U. S. Patent 2,345,376-8. Abst. in C. A. 38:4464 (1944).

173. _____, U. S. Patent 2,396,680-1. Abst. in C. A. 40:3626 (1946).

174. _____, U. S. Patent 2,433,593. Abst. in C. A. 43:2120 (1949).

175. _____, U. S. Patent 2,515,858. Abst. in C. A. 44:9170 (1950).

176. _____ and Dryden, U. S. Patent 2,511,427-8. Abst. in C. A. 44: 9124 (1950).

177. Cal. Res. Corp., Brit. Patent 640,148. Abst. in C. A. 45:1763 (1951).

178. _____, Brit. Patent 655,608. Abst. in C. A. 46:5312 (1952).

179. Calkins, J. Am. Chem. Soc., 60, 384-8 (1947).

180. _____ and Mattill, J. Am. Chem. Soc., 66, 239-42 (1944).

181. Campbell and Coppinger, J. Am. Chem. Soc., 74, 1469 (1952).

182. Cândea, Dobrescu and Gropsianu, Bul. Inst. Natl. Cercetăria Tehnol., 2, 98-109 (1947).

183. Capell, Ridenour and Stewart, U. S. Patent 2,636,002. Abst. in C. A. 47:6649 (1953).

184. _____, _____ and _____, U. S. Patent 2,646,362. Abst. in C. A. 47:1083 (1953).

185. Carlson and Brewer, Proc. Soc. Exptl. Biol. Med., 84, 6848 (1953).

186. Carola, Olii minerali grassi e saponi, colori vernici, 27, 13-20, 82-4 (1950).

187. Cartwright, Soap, Perfumery & Cosmetics, 24, 47-51 (1951).

188. Cathcart, Food Technol., 4, 209-18 (1950).

189. Cecil and Woodroof, Food Ind., 23, No. 2, 81-4, 223-4 (1951).

190. _____ and _____. Butylated hydroxyanisole as an antioxidant for salted peanuts, pecans and peanut butter. Georgia Agr. Expt. Sta. Bull. 265, 3-14 (1951).

191. Chalkley, U. S. Patent 2,366,179. Abst. in C. A. 39:1764 (1945).

192. Chamberlain and Walsh, Inst. intern. chim. Solvay, 8e Conseil chim., Univ. Bruxelles, Mécanisme de oxydation, Rapp. et disc., 1950, 155-64.

193. _____ and _____, Trans. Faraday Soc., 45, 1032-43 (1949).

194. Chang and Gisvold, J. Am. Pharm. Assoc., 38, 584-5 (1949).

195. _____ and Watts, Food Technol., 3, 332-6 (1949).

196. Chavez and Pechnik, Química, 1, 15-17 (1945).

197. Chemische Fabrik von Heyden A.-G., Belg. Patent 449,077. Abst. in C. A. 41:6740 (1947).

198. Chenicek, U. S. Patent 2,346,662-3. Abst. in C. A. 38:6544 (1944).

199. _____, U. S. Patent 2,464,291. Abst. in C. A. 43:4005 (1949).

200. _____, U. S. Patent 2,492,335. Abst. in C. A. 44:5496 (1950).

201. _____, U. S. Patent 2,492,336. Abst. in C. A. 44:5497 (1950).

202. _____, U. S. Patent 2,530,650. Abst. in C. A. 45:2193 (1951).

203. _____, U. S. Patent 2,533,205. Abst. in C. A. 45:2193 (1951).

204. _____, U. S. Patent 2,544,823. Abst. in C. A. 45:7345 (1951).

205. _____, U. S. Patent 2,553,441. Abst. in C. A. 45:8242 (1951).

206. _____, U. S. Patent 2,633,415. Abst. in C. A. 48:2096 (1954).

207. Chernozhukov and Tuzhetskiĭ, Neftyanoe Khoz., 25, No. 5, 48-53 (1947); Chem. Zentr. 1949, 702-3.

208. Chevreul, Ann. chim. phys., [3] 47, 209 (1856).

209. Chiang and Gisvold, J. Am. Pharm. Assoc., Sci. Ed., 41, 348-51 (1952).

210. Chilson, Martin and Whitnah, J. Dairy Sci., 33, 925-86 (1950).

211. Chipault, Hormel Inst., Univ. Minnesota Ann. Rept., 1951-52, 25-30.

212. Cignol, Rev. centro estud. farm. bioquím., 31, 51-72 (1941).

213. Clarkson and Pedersen, U. S. Patent 2,353,690. Abst. in C. A. 38: 6543 (1944).

214. Clausen, Lundberg and Burr, J. Am. Oil Chemists' Soc., 24, 403-4 (1947).

215. Clopton, J. Am. Oil Chemists' Soc., 30, 156-9 (1953).

216. Cocroft, Brennen and Manteuffel, U. S. Patent 2,480,449-50. Abst. in C. A. 43:9432 (1949).

217. Coe and Coe, U. S. Patent 2,397,920. Abst. in C. A. 40:3627 (1946).

218a. Cofield and Antle, Georgia Inst. Technol., State Eng. Expt. Sta., Research Engr., 1948-49, No. 5, 9-12, 24.

218b. Cohen and Wang, J. Am. Chem. Soc., 75, 5504 (1953).

219. Colomb, Ind. vernice, 5, 34-7 (1951).

220. Common, Can. Food Inds., 24, No. 8, 20-5 (1953).

221. Compagnie francaise de raffinage, Fr. Patent 977,966. Abst. in C. A. 47:570 (1953).

222. Conant, Chem. Rev., 3, 1 (1926).

223. Cook, C. D., J. Org. Chem., 18, 261-6 (1953).

224. Cook, E. W., Brit. Patent 591,836. Abst. in C. A. 42:3978 (1948).

225. _____, U. S. Patent 2,375,626. Abst. in C. A. 39:3452 (1945).

226. _____, U. S. Patent 2,467,295. Abst. in C. A. 43:5215 (1949).

227. _____ and Moss, U. S. Patent 2,434,396. Abst. in C. A. 42:3434 (1948).

228. _____, _____ and Hook, U. S. Patent 2,589,675. Abst. in C. A. 46:11239 (1952).

229. _____ and Thomas, U. S. Patent 2,344,392-3. Abst. in C. A. 38: 3829 (1944).

230. _____ and _____, U. S. Patent 2,347,592. Abst. in C. A. 39: 6135 (1945).

231. _____ and _____, U. S. Patent 2,365,938. Abst. in C. A. 39: 4751 (1945).

232. _____ and _____, U. S. Patent 2,373,811. Abst. in C. A. 40: 1030 (1946).

233. _____ and _____, U. S. Patent 2,385,957. Abst. in C. A. 40: 1023 (1946).

234. _____ and _____, U. S. Patent 2,393,889. Abst. in C. A. 40: 3010 (1946).

235. Coppock, U. S. Patent 2,665,254. Abst. in C. A. 48:4828 (1954).

236. Corubolo, Grims and Petričić, Acta Pharm. Jugoslav, 2, 58-67 (1952).

237. Cowie, Brit. Patent 688,703-4. Abst. in C. A. 48:8258 (1954).

238. Craig, U. S. Patent 2,388,041. Abst. in C. A. 40:1168 (1946).

239. Crampton and Mills, Can. J. Research, 23E, 131-7 (1945).

240. Crane, India Rubber J., 107, 657-8, 660 (1944).

241. Croux and Lemarchand, Rev. gén. caoutchouc, 28, 867-91 (1951).

242. Croxall and Van Hook, U. S. Patent 2,556,134. Abst. in C. A. 46: 525 (1952).

243. Cruess and Armstrong, Fruit Products J., 26, 327-8, 344 (1947).

244. Csuros and Hajós, Acta Chim. Acad. Sci. Hung., 1, 359-76 (1951).

245. Cultrera and Buffa, Conserve e deriv. agrumari, 1, No. 3, 3-5 (1952).

246. Cyphers and Michaels, U. S. Patent 2,654,712. Abst. in C, A. 48:994 (1954).

247. Dagne, U. S. Patent 2,425,085. Abst. in C. A. 41:6708 (1947).

248. Dalman, Afinidad, 28, 205-9 (1951).

249. Dam, Fette u. Seifen, 54, 633-5 (1952).

250. Davis, Rubber Age, 28, 179-80 (1947).

251. Dawson and Wasserman, U. S. Patent 2,502,436. Abst. in C. A. 44: 5909 (1950).

252. _____ and _____, U. S. Patent 2,502,708. Abst. in C. A. 44: 6436 (1950).

253. De Bataafsche, N. V., Petroleum Maatschappij, Brit. Patent 666,650. Abst. in C. A. 46:5882 (1952).

254. _____, Brit. Patent 692,261. Abst. in C. A. 48:10052 (1954).

255. _____, Dutch Patent 66,455. Abst. in C. A. 44:11079 (1950).

256. _____, Dutch Patent 66,833. Abst. in C. A. 45:4032 (1951).

257. _____, Dutch Patent 66,835. Abst. in C. A. 45:5919 (1951).

258. De Groes and Tamblyn, Modern Plastics, 29, No. 8, 127-8, 130, 132, 134, 136, 185-9 (1952).

259. de la Borbolla y Alcalá, Ion, 6, 415-22, 425 (1946).

260. _____, G.-Quijano and Ladrón, Grasas y aceites, 3, 173-9 (1952).

261. De Mytt and Reed, U. S. Patent 2,506,492. Abst. in C. A. 44:6586 (1950).

262. Denison and Condit, Ind. Eng. Chem., 37, 1102 (1945).

263. _____ and _____, Ind. Eng. Chem., 41, 944-8 (1949).

264. _____ and _____, U. S. Patent 2,346,153-5. Abst. in C. A. 38:5395 (1944).

265. _____ and _____, U. S. Patent 2,394,536. Abst. in C. A. 40: 2291 (1946).

266. _____ and _____, U. S. Patent 2,398,414. Abst. in C. A. 40: 3598 (1946).

267. _____ and _____, U. S. Patent 2,473,510-11. Abst. in C. A. 43:6820 (1949).

268. _____ and _____, U. S. Patent 2,528,346. Abst. in C. A. 45: 1339 (1951).

269. Deschamps, J. pharm. et chim., 4, 201 (1843).

270. Desnuelle, Massoni and Benoit-Micaelli, Bull. soc. chim. France, 1953, 595-9.

271. DeVilliers, U. S. Patent 2,347,814. Abst. in C. A. 39:613 (1945).

272. Dezĕlić, Grujić-Vasić and Bobarević, Bull. soc. Chimistes repub. pop. Bosnie et Herzegovine, 2, 55-67 (1953).

273. Dhar, J. Indian Chem. Soc., Ind & News Ed., 14, 175-6 (1951).

274. _____ and Aggarwal, J. Sci. Ind. Research, 8b, No. 1, 1-4 (1949).

275. Dickey and McNally, U. S. Patent 2,351,409. Abst. in C. A. 38:5415 (1944).

276. _____ and Normington, U. S. Patent 2,387,751. Abst. in C. A. 40: 1543 (1946).

277. Diemair, Ludwig and Weiss, Fette u. Seifen, 50, 349-54 (1943).

278. Digand and Fournier, Bull. soc. sci. hyg. aliment., 35, 116-22 (1947).

279. Dilworth, U. S. Patent 2,663,691. Abst. in C. A. 48:4215 (1954).

280. Dolgopol'skiĭ and Bartashaev, J. Applied Chem., 19, 1291-1302 (1946).

281. Donatelli, Biochim. terap. sper., 27, 288-302 (1940).

282. Donavan and Bean, U. S. Patent 2,597,915. Abst. in C. A. 47:435 (1953).

283a. Downing and Pedersen, U. S. Patent 2,426,766. Abst. in C. A. 42:355 (1948).

283b. Dox, J. Am. Chem. Soc., 47, 1473 (1925).

284. Dubouloz, Gasquet and Sebille, Compt. rend. soc. biol., 138, 670 (1944).

285. _____ and Hedde, Trav. membres soc. chim. biol., 24, 1137-44 (1942).

286. _____, _____ and Rousset, Compt. rend. soc. biol., 137, 457-8 (1943).

287. _____, Lagarde and Laurent, Oléagineux, 2, 242-6 (1947).

288. _____, Laurent and Jouve, Oléagineaux, 7, 265-71 (1952).

289. Dudani and Krishnamurti, Biochim. et Biophys. Acta, 13, 505-9 (1954).

290. Duffant, Bull. mens. ITERG, 4, 251-4 (1950).

291. Dugan, Hoffert, Blumer, Dabkiewicz and Kraybill, J. Am. Oil Chemists' Soc., 28, 493-5 (1951).

292. _____, Kraybill, Ireland and Vibrans, Food Technol., 4, 457-60 (1950).

293. _____ and Max, J. Am. Oil Chemists' Soc., 30, 452-4 (1953).

294. Dunn, Food Technol., 1, 371-83 (1947).

295. du Pont, E. I., de Nemours & Co., Brit. Patent 660,477. Abst. in C. A. 46:5879 (1952).

296. Dutton, U. S. Dept. Agr., Bur. Agr. Ind. Chem., AIC-198.

297. _____, Schwab, Moser and Cowan, J. Am. Oil Chemists' Soc., 25, 385-8 (1948).

298. Eby, U. S. Patent 2,523,100. Abst. in C. A. 44:11083 (1950).

299. _____, U. S. Patent 2,560,421. Abst. in C. A. 45:9259 (1951).

300. _____, U. S. Patent 2,614,914. Abst. in C. A. 47:3554 (1953).

301. _____ and Mikeska, U. S. Patent 2,462,616. Abst. in C. A. 43: 3606 (1949).

302. Eckert, U. S. Patent 2,663,690. Abst. in C. A. 48:4215 (1954).

303. Eddy, J. Econ. Entomol., 44, 109-11 (1951).

304. Edmonds, U. S. Patent 2,554,097. Abst. in C. A. 45:7348 (1951).

305. Egloff, Faragher and Morrell, Natl. Petroleum News, 21, No. 49, 40 (1929).

306. _____, Morrell, Lowry and Dryer, Ind. & Eng. Chem., 24, 1375 (1932).

307. Elder and Levenson, U. S. Patent 2,437,731. Abst. in C. A. 42:3977 (1948).

308. El-Sokkary and Ghoneim, Indian J. Dairy Sci., 4, 123-8 (1951).

309. Entwistle, Cole and Wooding, Textile Research J., 19, 609-24 (1949).

310. _____ and Voss, U. S. Patent 2,636,859. Abst. in C. A. 47:7205 (1953).

311. Ericks, U. S. Patent 2,423,643. Abst. in C. A. 42:3600 (1948).

312. Ericson and Gasparetto, Food Research, 18, 178-85 (1953).

313. Esh and Bhattacharya, Indian J. Physiol. and Allied Sci., 6, 43-7 (1952).

314. Esselen, Powers and Woodward, Ind. Eng. Chem., 37, 295-9 (1945).

315. Euler, Ahlström and Ek, Arkiv Kemi, Mineral Geol., 24A, No. 7, 1-12 (1946).

316. Evans, C. D., Cooney, Scholfield and Dutton, J. Am. Oil Chemists' Soc., 31, 295-7 (1954).

317. _____, Cowan and Schwab, U. S. Patent 2,645,648. Abst. in C. A. 47:10253 (1953).

318. _____, Schwab and Cooney, J. Am. Oil Chemists' Soc., 31, 9-12 (1954).

319. Evans, E. A., Inst. Petroleum, 32, 392-9 (1946).

320. Evans, H. C. and Young, U. S. Patent 2,380,299. Abst. in C. A. 39: 4516 (1945).

321. Evans, J. R. and Imperial Chemical Industries Ltd., Brit. Patent 579,675. Abst. in C. A. 41:1695 (1947).

322. Farrington, Clayton and Etzler, U. S. Patent 2,363,510-16. Abst. in C. A. 39:3924 (1945).

323. Feigenbaum, Nature, 157, 770-1 (1946).

324. Fernholz, J. Am. Chem. Soc., 60, 700-5 (1938).

325. Fiebler, Seifen-Öle-Fette-Wachse, 75, 89-92, 109-10 (1949).

326. Fieser, J. Am. Chem. Soc., 52, 5204 (1930).

327. Fife, Brit. Patent 387,314. Abst. in C. A. 41:6706 (1947).

328. Filer, Mattil and Longenecker, Oil & Soap, 21, 289-92 (1944).

329. Fincke, U. S. Patent 2,470,077. Abst. in C. A. 43:5801 (1949).

330. Findlay, Smith and Lea, J. Dairy Research, 14, 165-74 (1945).

331. Finley, U. S. Patent 2,347,546-7. Abst. in C. A. 39:613 (1945).

332. _____, U. S. Patent 2,379,290. Abst. in C. A. 39:4753 (1945).

333. _____ and Kirk, U. S. Patent 2,348,461. Abst. in C. A. 39:807 (1945).

334. _____ and _____, U. S. Patent 2,400,492. Abst. in C. A. 40: 5562 (1946).

335. Fiore and Sagarin, Am. Perfumer, 46, No. 7, 33-5 (1944).

336. _____ and _____, Am. Perfumer, 46, No. 8, 43-4, 91 (1944).

337. Fisher, Kaye and Bickford, Mfg. Confectioner, 29, No. 4, 24-6, 72 (1949).

338. _____, Kyame and Bickford, J. Am. Oil Chemists' Soc., 24, 340-3 (1947).

339. Fitzhugh and Nelson, Proc. Soc. Exptl. Biol. Med., 6, 195-8 (1946).

340. Flett, U. S. Patent 2,469,376. Abst. in C. A. 43:6845 (1949).

341. _____ and Seigle, U. S. Patent 2,494,650. Abst. in C. A. 44:3710 (1950).

342. Fonyo, Mfg. Confectioner, 37, No. 6, 41-2, 78 (1947).

343. Fossan, Tids. Kjemi, Bergvesen Met., 7, 12-15 (1947).

344. Francois and Geolier, Bull. mens. inform. ITERG, 4, 38-51 (1950).

345. _____ and Juillard, Bull. mens. inform. ITERG, 5, 186-90 (1951).

346. _____ and _____, Bull. mens. inform. ITERG, 6, 484-7 (1952).

347. _____ and Sergent, Bull. mens. inform. ITERG, 3, 217-19 (1949).

348. Frank, Badertscher and Berger, U. S. Patent 2,388,400. Abst. in C. A. 40:1027 (1946).

349. Franz, U. S. Patent 2,361,538. Abst. in C. A. 39:2292 (1945).

350. Freuler, U. S. Patent 2,364,283-4. Abst. in C. A. 39:4475 (1945).

351. Fukuba, Eiyô to Shokuryô (J. Japan Soc. Food Nutrition), 4, 192-201 (1952).

352. Fuller, U. S. Patent 2,336,006. Abst. in C. A. 38:3832 (1944).

353. _____, U. S. Patent 2,350,746. Abst. in C. A. 38:5396 (1944).

354. _____ and Angel, U. S. Patent 2,455,668. Abst. in C. A. 43:1561 (1949).

355. _____ and Hamilton, U. S. Patent 2,326,938. Abst. in C. A. 38: 860 (1944).

356. _____, Redman and Berger, U. S. Patent 2,427,272. Abst. in C. A. 42:358 (1948).

357. Funabashi, Koryo (Aromatics), No. 22, 38-45 (1952).

358. Galinde, Tesis quím, Univ. Chile, 3, 23-36 (1951).

359. Galli and Blamo, Quimica ind., 1, 91-101 (1947).

360. Garrett and Bosshardt. Effect of various storage conditions on the stability of carotenoid pigments in butter. New Jersey Agr. Expt. Sta. Bull. 710 (1944).

361. Gates, Can. Patent 423,653. Abst. in C. A. 39:766 (1945).

362. _____, U. S. Patent 2,352,950. Abst. in C. A. 38:6131 (1944).

363. Gaylor, U. S. Patent 2,370,787. Abst. in C. A. 39:5470 (1945).

364. Gemmill, Food Eng., 24, No. 5, 102-5 (1952).

365. Gero, Compt. rend., 238, 959-61 (1954).

366. Giacoboni-Vercesi, Mondo latte, 1951, 208, 211, 213-4, 217.

367. Giammaria and Reiff, U. S. Patent 2,386,206. Abst. in C. A. 40:5237 (1946).

368. Gibbs, U. S. Patent 2,342,135-7. Abst. in C. A. 38:4834 (1944).

369. _____, U. S. Patent 2,359,360. Abst. in C. A. 39:1567 (1945).

370. _____, U. S. Patent 2,362,479. Abst. in C. A. 39:2668 (1945).

371. _____, U. S. Patent 2,366,018. Abst. in C. A. 39:4516 (1945).

372. _____, U. S. Patent 2,378,698. Abst. in C. A. 39:4096 (1945).

373. _____, U. S. Patent 2,393,156. Abst. in C. A. 40:3133 (1946).

374. _____, U. S. Patent 2,400,500. Abst. in C. A. 40:5457 (1946).

375. _____, U. S. Patent 2,408,391. Abst. in C. A. 41:1248 (1947).

376. Gilbert, U. S. Patent 2,348,290. Abst. in C. A. 39:1533 (1945).

377. Gill, U. S. Patent 2,430,050. Abst. in C. A. 42:1044 (1948).

378. Gisvold, U. S. Patent 2,421,117. Abst. in C. A. 41:4895 (1947).

379. _____, U. S. Patent 2,421,118. Abst. in C. A. 41:4896 (1947).

380. _____, Bope and Rogers, J. Am. Pharm. Assoc., Sci. Ed., 37, 232-4 (1948).

381. _____, Buelow and Carlson, J. Am. Pharm. Assoc., 35, 188-91 (1946).

382. Gleim and Chenicek, U. S. Patent 2,535,058. Abst. in C. A. 45:2191 (1951).

383. Glimm and Nowack, Fette u. Seifen, 50, 217-18 (1943).

384. Golumbic, J. Am. Chem. Soc., 63, 1142, 1163, 1279 (1941).

385. _____, Oil & Soap, 19, 181 (1942).

386. _____, Oil & Soap, 20, 105 (1943).

387a. _____, Oil & Soap, 23, 184-6 (1946).

387b. Gomberg and Berger, Ber., 36, 1088 (1903).

388. Goodrich, B. F., Co., Brit. Patent 561,999. Abst. in C. A. 40:487 (1946).

389. _____, Brit. Patent 563,479. Abst. in C. A. 40:2683 (1946).

390. _____, Brit. Patent 620,314. Abst. in C. A. 43:6241 (1949).

391. Goppel, Rumscheidt and Hackmann, U. S. Patent 2,578,653. Abst. in C. A. 46:2838 (1952).

392. Goren and Adelson, U. S. Patent 2,511,630. Abst. in C. A. 44:8634 (1950).

393. G.-Quijano, Ladrón and de la Borbolla y Alcalá, Grasas y aceites, 4, 119-22 (1953).

394. Greenbank, Proc. 12th Intern. Dairy Congr., 2, 284-91 (1949).

395. Gresham, U. S. Patent 2,376,354. Abst. in C. A. 39:3703 (1945).

396. Gribbins, U. S. Patent 2,462,633. Abst. in C. A. 43:3542 (1949).

397. _____, U. S. Patent 2,519,755. Abst. in C. A. 45:905 (1951).

398. _____ and Dittmar, U. S. Patent 2,563,835. Abst. in C. A. 45: 9769 (1951).

399. _____ and _____, U. S. Patent 2,564,106. Abst. in C. A. 45: 9769 (1951).

400. Griewahn and Daubert, J. Am. Oil Chemists' Soc., 25, 26-7 (1948).

401. Groote and Keiser, U. S. Patent 2,581,367. Abst. in C. A. 46:1176 (1952).

402. Guest, U. S. Patent 2,561,468. Abst. in C. A. 47:1189 (1953).

403. Gunther, Kohn and Stone, U. S. Patent 2,500,147. Abst. in C. A. 44: 4632 (1950).

404. György, U. S. Patent 2,420,238. Abst. in C. A. 41:5233 (1947).

405. _____, U. S. Patent 2,536,865. Abst. in C. A. 45:1362 (1951).

406. _____ and Tomarelli, J. Biol. Chem., 154, 317-24 (1944).

407. _____, Williamson and Stiller, U. S. Patent 2,456,937. Abst. in C. A. 43:1880 (1949).

408. Gzemski, U. S. Patent 2,326,140. Abst. in C. A. 38:1353 (1944).

409. Haberland, Caspe and Manz, Ger. Patent 851,344. Abst. in C. A. 47: 5437 (1953).

410. Hadert, Farbe u. Lack, 56, 349-51 (1950).

411. Hald, Gad and Deans, U. S. Patent 2,647,145. Abst. in C. A. 48:8258 (1954).

412. Hall, A. M. and Woolman, U. S. Patent 2,651,618. Abst. in C. A. 48: 1050 (1954).

413. Hall, L. A., U. S. Patent 2,493,288. Abst. in C. A. 44:3632 (1950).

414. _____, U. S. Patent 2,500,543. Abst. in C. A. 44:5036 (1950).

415. _____, U. S. Patent 2,518,233. Abst. in C. A. 44:10210 (1950).

416. _____ and Sair, U. S. Patent 2,511,802-4. Abst. in C. A. 44:8562 (1950).

417. Hamblet, U. S. Patent 2,409,678. Abst. in C. A. 41:1121 (1947).

418. Hamilton and Pederson, U. S. Patent 2,461,894. Abst. in C. A. 43: 3839 (1949).

419. Hammond, J. Am. Chem. Soc., 72, 3737 (1950).

420. _____, Boozer, Hamilton, and Sen. The effects of varying solvent and the mechanism of uninhibited chain termination; Mechanism of inhibitor action in benzene and chlorobenzene solutions. Unpublished research. Iowa State College, Ames, Iowa (1954).

421. _____, Sen and Boozer. The efficiency of radical production from azo-bis-isobutyronitrile. Unpublished research. Iowa State College, Ames, Iowa (1954).

422. Hardman, U. S. Patent 2,375,168. Abst. in C. A. 39:3460 (1945).

423. Harman, U. S. Patent 2,582,695. Abst. in C. A. 46:3791 (1952).

424. Hart and Armstrong, U. S. Patent 2,361,543. Abst. in C. A. 39:2427 (1945).

425. Hartman and White, New Zealand J. Sci. Technol., 35B, 254-8 (1953).

426. Hartmann, Proc. 11th Intern. Cong. Pure & Applied Chem., London, 1947, 3, 93-6 (1951).

427. Hartough, U. S. Patent 2,492,632. Abst. in C. A. 44:3031 (1950).

428. _____, U. S. Patent 2,566,611. Abst. in C. A. 45:10561 (1951).

429. Harvel Corp., Brit. Patent 627,927. Abst. in C. A. 44:4503 (1950).

430. Hashimoto and Kobayashi, Japan Patent 174,923. Abst. in C. A. 43: 6966 (1949).

431. Hastings, Southern Fisherman, 13, No. 10, 114 (1953).

432. Haward and Borrows, U. S. Patent 2,650,899. Abst. in C. A. 48:1062 (1954).

433. Haworth, Lambert and Imperial Chem. Co. Ltd., Brit. Patent 651,368. Abst. in C. A. 45:7372 (1951).

434. Hayashi, J. Soc. Rubber Ind. Japan, 21, 162-3 (1948).

435. Heftmann, J. Am. Oil Chemists' Soc., 24, 404-9 (1947).

436. Heiks and Croxton, Ind. Eng. Chem., 43, 876-84 (1951).

437. Heimann, Z. Lebensm.-Untersuch. u. -Forsch., 88, 586-93 (1948).

438. _____, Heimann, Gremminger and Holland, Fette u. Seifen, 55, 394-8 (1953).

439. Heinrich, U. S. Patent 2,641,548. Abst. in C. A. 47:8288 (1953).

440. Henn, U. S. Patent 2,458,376. Abst. in C. A. 43:2106 (1949).

441. Hérisset, Bull. soc. chim. biol., 30, 202-13 (1948).

442. _____, Compt. rend., 223, 47-9 (1946).

443. Herlocker, Kleinholz and Watkins, U. S. Patent 2,360,323. Abst. in C. A. 39:1535 (1945).

444. Hermann, Vial and Chatonnet, Compt. rend. soc. biol., 139, 114 (1945).

445. Higgins and Black, Oil & Soap, 21, 277-9 (1944).

446. Hilditch, Chemistry & Industry, 1944, 67-71.

447. Hill, U. S. Patent 2,635,042. Abst. in C. A. 47:6644 (1953).

448. _____ and Baldwin, U. S. Patent 2,576,458. Abst. in C. A. 46: 1745 (1952).

449. _____ and DePree, U. S. Patent 2,651,620-3. Abst. in C. A. 48: 1051 (1954).

450. _____ and _____, U. S. Patent 2,651,667. Abst. in C. A. 48: 7332 (1954).

451. _____ and Welp, U. S. Patent 2,657,982-3. Abst. in C. A. 48:2289 (1954).

452. Himel and Bailey, U. S. Patent 2,439,734. Abst. in C. A. 43:1176 (1949).

453. Hodgins and Hovey, Brit. Patent 642,453. Abst. in C. A. 46:133 (1952).

454. Hoertz, U. S. Patent 2,662,867. Abst. in C. A. 48:4252 (1954).

455. Hoffmann-La Roche, Inc., Brit. Patent 585,828. Abst. in C. A. 41: 6895 (1947).

456. Holgate, Moyer and Pederson, Fruit Products J., 28, 100-2, 112 (1948).

457. Hollibaugh, U. S. Patent 2,665,253. Abst. in C. A. 48:4828 (1954).

458. Hollis, U. S. Patent 2,530,769. Abst. in C. A. 45:3418 (1951).

459. Holly, Shunk and Folkers, U. S. Patent 2,621,175. Abst. in C. A. 47:10013 (1953).

460. Hoock and Kleinholz, U. S. Patent 2,515,222. Abst. in C. A. 44:8634 (1950).

461. Hook and Beegle, U. S. Patent 2,627,523. Abst. in C. A. 47:5110 (1953).

462. _____ and _____, U. S. Patent 2,657,900. Abst. in C. A. 48: 5484 (1954).

463. _____ and Moss, U. S. Patent 2,531,129. Abst. in C. A. 45:2194 (1951).

464. _____ and _____, U. S. Patent 2,555,920. Abst. in C. A. 46: 3067 (1952).

465. _____ and _____, U. S. Patent 2,577,966. Abst. in C. A. 46: 2341 (1952).

466. _____ and _____, U. S. Patent 2,586,655-6. Abst. in C. A. 46: 8144 (1952).

467. Houchin, Biol. Antioxidants, Trans. 1st Conf., 1946, 60-2.

468. Hove, J. Biol. Chem., 156, 633-42 (1944).

469. _____ and Hove, J. Biol. Chem., 156, 623-32 (1944).

470. Howard, U. S. Patent 2,322,938. Abst. in C. A. 38:189 (1944).

471. Howland, U. S. Patent 2,458,780. Abst. in C. A. 43:3042 (1949).

472. _____, U. S. Patent 2,460,177. Abst. in C. A. 43:2803 (1949).

473. _____ and Hunter, U. S. Patent 2,419,354. Abst. in C. A. 41:4672 (1947).

474. _____ and _____, U. S. Patent 2,466,810. Abst. in C. A. 43: 4891 (1949).

475. _____ and Paul, Can. Patent 427,656. Abst. in C. A. 39:4257 (1945).

476. _____ and _____, U. S. Patent 2,377,423. Abst. in C. A. 39: 4257 (1945).

477. Hughes, U. S. Patent 2,363,001. Abst. in C. A. 39:3926 (1945).

478. _____, U. S. Patent 2,553,588. Abst. in C. A. 45:7348 (1951).

479. _____ and Bartleson, U. S. Patent 2,553,586. Abst. in C. A. 45: 7348 (1951).

480. Hunter, B. A., U. S. Patent 2,488,975. Abst. in C. A. 44:5633 (1950).

481. _____, U. S. Patent 2,587,477. Abst. in C. A. 46:4266 (1952).

482. _____, U. S. Patent 2,605,250. Abst. in C. A. 46:10676 (1952).

483. _____, U. S. Patent 2,632,770. Abst. in C. A. 47:7250 (1953).

484. Hunter, L. and Barnes, J. Chem. Soc., 1928, 2055.

485. Hunter, W. and Downing, J. Soc. Chem. Ind., 68, 3624 (1949).

486. Husaini and Saletore, J. Sci. Ind. Research (India), 12B, 408-10 (1953).

487. Iinuma, Japan Patent 1,318. Abst. in C. A. 46:7811 (1952).

488. Inagaki, Nôgaku, 1, 237-41 (1947).

489. Inglett, Univ. Microfilms, Pub. No. 4073. Abst. in Dissertation Abstracts, 12, 565-6 (1952).

490. Ingram, Brit. Patent 675,585. Abst. in C. A. 47:1420 (1953).

491. _____, U. S. Patent 2,374,098. Abst. in C. A. 39:5117 (1945).

492. _____, U. S. Patent 2,511,063. Abst. in C. A. 44:8166 (1950).

493. Ipatieff and Pines, U. S. Patent 2,557,505. Abst. in C. A. 46:3083 (1952).

494. _____ and _____, U. S. Patent 2,631,174. Abst. in C. A. 48: 1442 (1954).

495. Jacobs, U. S. Patent 2,403,284. Abst. in C. A. 40:5914 (1946).

496. Jacquemain and Berger, Compt. rend., 227, 436-7 (1948).

497. Janecke, Arzneimittel-Forsch, 3, 574-86, 632-9 (1953).

498. _____, Deut. Lebensmittel-Rundschau, 50, 65-9 (1954).

499. Jarowski, U. S. Patent 2,455,256. Abst. in C. A. 43:1586 (1949).

500. _____ and Stiller, U. S. Patent 2,455,254. Abst. in C. A. 43: 2399 (1949).

501. Jen, Tong, Lin and Ma, J. Chinese Chem. Soc., 11, 25-33 (1944).

502. Joanen, U. S. Patent 2,547,396. Abst. in C. A. 46:732 (1952).

503. Johnson, G. C., U. S. Patent 2,560,956. Abst. in C. A. 45:8755 (1951).

504. _____ and Johnson, D. K., Food Technol., 6, 242-5 (1952).

505. Johnson, H. G., U. S. Patent 2,452,535. Abst. in C. A. 43:2230 (1949).

506. Jones, A. R. and Smith, U. S. Patent 2,627,511. Abst. in C. A. 47: 4599 (1953).

507. _____ and _____, U. S. Patent 2,647,824. Abst. in C. A. 47: 10218 (1953).

508. Jones, D. G., Brit. Patent 687,293. Abst. in C. A. 48:3385 (1954).

509. _____ and Cowie, Brit. Patent 679,504. Abst. in C. A. 47:10009 (1953).

510. _____ and _____, Brit. Patent 699,349. Abst. in C. A. 48: 6683 (1954).

511. _____, Robertson and Imperial Chemical Industries Ltd., Brit. Patent 675,285. Abst. in C. A. 47:4899 (1953).

512. Jones, M. C. K., Jones, A. R. and Strickland, Ind. Eng. Chem., 44, 2721-5 (1952).

513. Jones, R. H. and Moody, U. S. Patent 2,636,858. Abst. in C. A. 47: 7206 (1953).

514. Jordi, Folch-Pi and Sperry, Ann. Rev. Biochem., 17, 147-68 (1948).

515. Jorissen, Rec. trav. chim., 64, 147-58, 284-8 (1945).

516. _____, Rec. trav. chim., 65, 5-9 (1946).

517. Kahan, J. Assoc. Offic Agr. Chemists, 35, 186-93 (1952).

518. Kaloyeareas, J. Am. Oil Chemists' Soc., 24, 39-41 (1947).

519. Kambara, Japan Patent 1,320. Abst. in C. A. 46:7813 (1952).

520. Kameth and Magar, J. Indian Chem. Soc., 30, 335-41 (1953).

521. Kapeller, Zucker- u. Süsswaren-Wirtsch, 3, No. 22, 41-3 (1950).

522. Karrman, Iva, 18, 79-88 (1947).

523. _____, Svensk Kem. Tid., 58, 92-100 (1946).

524. Katsui, Vitamins (Japan), 5, 457-9 (1952).

525. _____, Vitamins (Japan), 6, 69-71 (1953).

526. _____ and Kuyama, Vitamins (Japan), 4, 47-9, 422-4 (1951).

527. _____ and _____, Vitamins (Japan), 5, 34-41, 342-5 (1952).

528. Katsuno, J. Soc. Chem. Ind. Japan, 44, 903-7 (1941).

529. Kaufmann and Wolf, Fette u. Seifen, 50, 218-20 (1943).

530. Kavanagh, Farrington and Clayton, U. S. Patent 2,344,988. Abst. in C. A. 38:4433 (1944).

531. Kawai, Japan Patent 172,915. Abst. in C. A. 46:1723 (1952).

532. _____, Shimizen and Suzuki, J. Pharm. Soc. Japan, 72, 553-6 (1952).

533. Kehe, U. S. Patent 2,670,340. Abst. in C. A. 48:7926 (1954).

534. _____ and Jensen, U. S. Patent 2,636,905. Abst. in C. A. 48:5222 (1954).

535. _____ and Shelley, U. S. Patent 2,530,774. Abst. in C. A. 45: 2704 (1951).

536. Kellog, U. S. Patent 2,497,061. Abst. in C. A. 44:4712 (1950).

537. Kenyon and Proctor, Sci. Agr., 16, 365-71 (1951).

538. Kern, Antoshkim and Maiese, Ind. Eng. Chem., 41, 2849-53 (1949).

539. _____, Jockurch and Wolfram, Makromol. Chem., 3, 223-46 (1949).

540. Kesterson and McDuff, Am. Perfumer Essent. Oil Rev., 54, 285-7 (1949).

541. Kirshenbaum and Rudel, U. S. Patent 2,654,711. Abst. in C. A. 48: 7670 (1954).

542. Kitchen, U. S. Patent 2,537,636. Abst. in C. A. 45:3644 (1951).

543. _____, U. S. Patent 2,605,252. Abst. in C. A. 47:9044 (1953).

544. _____, U. S. Patent 2,647,152. Abst. in C. A. 47:11794 (1953).

545. _____ and Ambelang, U. S. Patent 2,560,028. Abst. in C. A. 45: 8800 (1951).

546. Klose, Mecchi and Hanson, Food Technol., 6, 308-11 (1952).

547. Kluge and Knowles, U. S. Patent 2,469,469. Abst. in C. A. 43:6406 (1949).

548. _____ and _____, U. S. Patent 2,526,755. Abst. in C. A. 45: 1338 (1951).

549. _____ and Patterson, U. S. Patent 2,452,319-20. Abst. in C. A. 43:1176 (1949).

550. Knowles, McCoy and Patterson, U. S. Patent 2,417,305. Abst. in C. A. 41:3613 (1947).

551. Komarik and Hall, U. S. Patent 2,553,533. Abst. in C. A. 45:7272 (1951).

552. Korner, U. S. Patent 2,486,177. Abst. in C. A. 44:5496 (1950).

553. _____ and Loomis, U. S. Patent 2,394,456. Abst. in C. A. 40:2243 (1946).

554. Kosolapoff, U. S. Patent 2,355,593. Abst. in C. A. 39:92 (1945).

555. Kozin and Bessonov, Voprosy Pitaniya, 10, No. 5-6, 24-9 (1941).

556. Kraft and Wanderstock, Food Inds., 22, 65-9 (1950).

557. Krauss, Angew. Chem., 61, 412 (1949).

558. Kraybill and Beadle, U. S. Patent 2,521,856. Abst. in C. A. 45:292 (1951).

559. _____ and Dugan, J. Agr. Food Chem., 2, 81-4 (1954).

560. _____, _____, Beadle, Vibrans, Swartz and Kezabek, J. Am. Oil Chemists' Soc., 26, 449-53 (1949).

561. Krein, Izvest. Vsesoyuz. Teplotekh Inst., 14, No. 3, 15-21 (1941); Chem. Zentr. 1943, I, 1237-8.

562. Kring, Dansk Tids. Farm., 24, 211-27 (1950).

563. Krȍger, Erdȍl u. Kolile, 1, 389-96 (1948).

564. Kuhrt, U. S. Patent 2,681,281-3. Abst. in C. A. 48:10361 (1954).

565. Kumeno, J. Soc. Rubber Ind. Japan, 14, 441-5 (1941).

566. Kummerow, Octo, Jacobson and Randolf, Biol. Antioxidants, Trans. 4th Conf., 1949, 148-73.

567. Kurth and Chan, J. Am. Oil Chemists' Soc., 28, 433-6 (1951).

568. Kuz'minskiĭ and Angert, Doklady Akad. Nauk, S.S.S.R., 82, 747-50 (1952).

569. _____ and Lezhnev, Khim. i Fiz.-Khim. Vysokomolekul. Soedineniĭ, Doklady 7-oĭ Konf. Vysokomolekul. Soedineniyam 1952, 90-8.

570. Laban, Tesis quím. Univ. Chile, 2, 17-32 (1950).

571. Ladd and Harvey, U. S. Patent 2,553,417. Abst. in C. A. 45:6865 (1951).

572. _____ and _____, U. S. Patent 2,609,376. Abst. in C. A. 47: 7540 (1953).

573. Lakritz, Mfg. Confectioner, 23, No. 9, 18-19 (1943).

574. Lategan, J. S. African Chem. Inst., 1, 39-60 (1948).

575. Lea, Chemistry & Industry, 1952, 178-83.

576. _____, J. Soc. Chem. Ind., 63, No. 2, 55-7 (1944).

577. _____, J. Soc. Chem. Ind., 63, 107-12 (1944).

578. _____ and Smith, Proc. 12th Intern. Dairy Congr., 2, 341-9 (1949).

579. Le Bras, Compt. rend., 217, 297-9 (1943).

580. _____, Rev. gen. caoutchouc, 21, 125-6 (1944).

581a. _____ and Le Foll, Compt. rend., 231, 145-7 (1950).

581b. Leffler and Alders, J. Am. Chem. Soc., 76, 1425 (1954).

582. Le Foll, Rev. gén. caoutchouc, 29, 114-17 (1952).

583. Lehman, Some toxicological reasons why certain chemicals may or may not be permitted as food additives. Assoc. Food & Drug Officials U. S., Quart. Bull., 14, 82-98 (1950).

584. _____, Chemicals in foods: A report of the Assoc. of Food & Drug Officials on current developments. Assoc. Food & Drug Officials U. S., Quart. Bull., 15, 82-9 (1951).

585. _____, Fitzhugh, Nelson and Woodward, Advances in Food Research, 3, 197-208 (1951).

586. Lehmann and Watts, J. Am. Oil Chemists' Soc., 28, 475-7 (1951).

587. Lemon, Knapp and Allman, Can. J. Research, 28F, 453-60 (1950).

588. Levesque, U. S. Patent 2,525,416. Abst. in C. A. 45:1623 (1951).

589. Lewis, F. M. and Matheson, J. Am. Chem. Soc., 71, 747 (1949).

590. Lewis, H. F., U. S. Patent 2,334,564. Abst. in C. A. 38:3812 (1944).

591. _____, Buchanan, Fronmuller and Kurth, Ind. Eng. Chem., 37, 988-90 (1945).

592. _____, _____, Kurth and Fronmuller, Ind. Eng. Chem., 37, 1108-11 (1945).

593. Liander and Ericson, ASEA Journal, 7092E, 14 pp. (1946).

594. Lieber and Cashman, U. S. Patent 2,454,394. Abst. in C. A. 43:2424 (1949).

595. Lincoln and Byrkit, U. S. Patent 2,371,631. Abst. in C. A. 39:5470 (1945).

596. _____ and _____, U. S. Patent 2,395,889. Abst. in C. A. 40: 2974 (1946).

597. _____ and _____, U. S. Patent 2,418,358. Abst. in C. A. 41: 3957 (1947).

598. _____ and _____, U. S. Patent 2,421,631. Abst. in C. A. 41: 6710 (1947).

599. _____ and _____, U. S. Patent 2,460,301. Abst. in C. A. 43: 2765 (1949).

600. _____, _____ and Steiner, U. S. Patent 2,367,133. Abst. in C. A. 39:3425 (1945).

601. _____ and Steiner, U. S. Patent 2,433,853. Abst. in C. A. 42: 2097 (1948).

602. Lindow and Thompson, U. S. Patent 2,382,242. Abst. in C. A. 39:4998 (1945).

603. Lineweaver, Anderson and Hanson, Food Technol., 6, 1-3 (1952).

604. Lips, Can. J. Research, 27F, 373-81 (1949).

605. _____, Can. J. Research, 28F, 451-2 (1950).

606. _____, Foods in Canada, 12, No. 6, 9-10, 12, 16 (1952).

607. _____, Grace and Ziegler, Can. J. Technol., 30, 1-8 (1952).

608. _____ and McFarlane, Oil & Soap, 20, 193-6 (1943).

609. List of antioxidants proposed for the preservation of edible fats, U. S. Dept. Agr., Southern Regional Research Lab. AIC-54 (1944).

610. Loane and Gaynor, U. S. Patent 2,363,133. Abst. in C. A. 39:3926 (1945).

611. _____ and Mixon, U. S. Patent 2,546,552. Abst. in C. A. 45:5921 (1951).

612. Loiseleur, Compt. rend., 230, 1901-2 (1950).

613. Longenecker and Danbert, Ann. Rev. Biochem., 14, 113-44 (1945).

614. Lonza Elektrizitätswerke und Chemische Fabriken A.-G., Swiss Patent 247,835. Abst. in C. A. 43:8076 (1949).

615. Lory, Schuster and Ferrand, Ann. pharm. franc., 7, 537-41 (1949).

616. Lovern, J. Soc. Chem. Ind., 63, 13-15 (1944).

617. _____, Oil & Soap, 23, 40-5 (1946).

618. Loury, Chemie & industrie, 53, 4-8 (1945). Bull. mat. grasses inst. colonial Marseille, 28, 138-47 (1944).

619. Lowry, U. S. Patent 2,387,920. Abst. in C. A. 40:446 (1946).

620. _____, Egloff, Morrell and Dryer, Ind. & Eng. Chem., 25, 804 (1933).

621. Lukesiewicz and Sachanen, U. S. Patent 2,562,238. Abst. in C. A. 45:9853 (1951).

622. Lundberg, Biol. Antioxidants, Trans. 1st Conf. 1946, 26-36.

623. _____, U. S. Patent 2,523,127. Abst. in C. A. 44:10959 (1950).

624. _____, Dockstader and Halvorson, J. Am. Oil Chemists' Soc., 24, 89-92 (1947).

625. _____ and Halvorson, Proc. Inst. Food Tech. 1945, 115-25.

626. _____, _____ and Burr, Oil & Soap, 21, 33-5 (1944).

627. Luten, Brit. Patent 572,012. Abst. in C. A. 41:6707 (1947).

628. _____, U. S. Patent 2,351,347. Abst. in C. A. 38:6090 (1944).

629. _____, U. S. Patent 2,410,829. Abst. in C. A. 41:1090 (1947).

630. _____, Ballard and Schwarzer, U. S. Patent 2,602,821-2. Abst. in C. A. 47:7544 (1953).

631. Luther and Cragwall, Food Industries, 18, 690-2, 794, 796, 798, 800 (1946).

632. Lützkendorf, Seifen-Öle-Fette-Wachse, 77, 221-3 (1951).

633. Lyon and Crouch, U. S. Patent 2,527,948. Abst. in C. A. 45:2966 (1951).

634. Mack and Bickford, J. Am. Oil Chemists' Soc., 29, 428-30 (1952).

635. MacKenzie, Cosmo, Jensen and Holman, Biological antioxidants New York: Josiah Macy, Jr., Foundation, 1950, 181 pp.

636. Magoffin, U. S. Patent 2,607,745-6. Abst. in C. A. 46:11722 (1952).

637. Mahon and Chapman, J. Am. Oil Chemists' Soc., 30, 34-9 (1953).

638. _____ and _____, J. Am. Oil Chemists' Soc., 31, 108-12 (1954).

639. Mallette and Von Haam, Arch. Ind. Hyg. Occupational Med., 5, 311-17 (1952).

640. Mankowich, U. S. Patent 2,650,252. Abst. in C. A. 48:1050 (1954).

641. _____, U. S. Patent 2,657,236. Abst. in C. A. 48:4248 (1954).

642. _____, U. S. Patent 2,663,734. Abst. in C. A. 48:4248 (1954).

643. _____, U. S. Patent 2,666,792-3. Abst. in C. A. 48:5543 (1954).

644. Mann, Trans. Inst. Rubber Ind., 27, 232-48 (1951).

645. Marcuse, Fette u. Seifen, 54, 530-9 (1952).

646. Mathiesen, U. S. Patent 2,461,651. Abst. in C. A. 43:3540 (1949).

647. Matthews, U. S. Patent 2,647,873. Abst. in C. A. 47:11721 (1953).

648. Mattil and Black, J. Am. Oil Chemists' Soc., 24, 325-7 (1947).

649. _____, Filer and Longenecker, Oil & Soap, 21, 160-1 (1944).

650. Mattill, Ann. Rev. Biochem., 16, 177-92 (1947).

651. _____, J. Biol. Chem., 141, 90 (1931).

652. _____, Oil & Soap, 22, 1-3 (1945).

653. _____ and Golumbic, U. S. Patent 2,333,655-8. Abst. in C. A. 38: 2519 (1944).

654. Mattson, U. S. Patent 2,543,325. Abst. in C. A. 45:4034 (1951).

655. May, U. S. Patent 2,409,877. Abst. in C. A. 41:1096 (1947).

656. _____, U. S. Patent 2,538,696. Abst. in C. A. 45:3590 (1951).

657. Mayberry, Confectioners J., Nov. 1949.

658. McCarthy, U. S. Patent 2,662,057. Abst. in C. A. 48:4215 (1954).

659. McCleary, U. S. Patent 2,363,134. Abst. in C. A. 39:3925 (1945).

660. _____, U. S. Patent 2,409,296. Abst. in C. A. 41:1095 (1947).

661. _____, U. S. Patent 2,440,375. Abst. in C. A. 42:7031 (1948).

662. _____ and Devaney, U. S. Patent 2,584,278. Abst. in C. A. 47: 615 (1953).

663. _____ and Morris, U. S. Patent 2,380,658. Abst. in C. A. 40:754 (1946).

664. McConnell, Am. Perfumer, 50, 346-9 (1947).

665. _____, Am. Perfumer Essent. Oil Rev., 50, 241-3 (1947).

666. _____ and Esselen, J. Am. Oil Chemists' Soc., 24, 6-13 (1947).

667. McCracken, U. S. Patent 2,518,351. Abst. in C. A. 45:4034 (1951).

668. McDermott, U. S. Patent 2,436,589. Abst. in C. A. 42:3950 (1948).

669. _____, U. S. Patent 2,500,195. Abst. in C. A. 44:5576 (1950).

670. _____, U. S. Patent 2,529,303. Abst. in C. A. 45:1763 (1951).

671. _____, U. S. Patent 2,545,158. Abst. in C. A. 45:4440 (1951).

672. _____, U. S. Patent 2,591,577. Abst. in C. A. 46:6374 (1952).

673. _____, U. S. Patent 2,599,341. Abst. in C. A. 46:8362 (1952).

674. _____, U. S. Patent 2,610,182. Abst. in C. A. 47:1377 (1953).

675. _____, U. S. Patent 2,631,132. Abst. in C. A. 47:5111 (1953).

676. McHan, U. S. Patent 2,479,583. Abst. in C. A. 44:246 (1950).

677. McNab and Bartlett, U. S. Patent 2,460,025. Abst. in C. A. 43:4458 (1949).

678. _____, Hakala and McDermott, U. S. Patent 2,552,570. Abst. in C. A. 45:7785 (1951).

679. _____ and Rogers, U. S. Patent 2,556,848. Abst. in C. A. 45:9257 (1951).

680. _____ and Watkins, U. S. Patent 2,493,986. Abst. in C. A. 44: 11084 (1950).

681. Meier and Mebes, Farbe u. Lack, 58, 215-21 (1952).

682. Menezes and Banerjee, J. Indian Inst. Sci., 27A, 7-30 (1945).

683. Mester, Science et inds. phot., 23, 337-41 (1952).

684. Meyer and McShan, Biol. Antioxidants, Trans. 3rd Conf. 1948, 115-30.

685. Michaelis, Biol. Antioxidants, Trans. 3rd Conf. 1948, 11-23.

686a. _____, Chem. Rev., 16, 243 (1935).

686b. Michalowska, Przemyst Chem., 6 (29), 12-20 (1950).

687. Mikeska, U. S. Patent 2,461,335. Abst. in C. A. 43:4460 (1949).

688. _____, U. S. Patent 2,605,278. Abst. in C. A. 46:10650 (1952).

689. _____, U. S. Patent 2,656,705. Abst. in C. A. 48:3024 (1954).

690. _____ and Kittleson, U. S. Patent 2,415,833. Abst. in C. A. 41: 3288 (1947).

691. _____ and _____, U. S. Patent 2,530,339. Abst. in C. A. 45: 2195 (1951).

692. _____, _____ and Smith, U. S. Patent 2,453,850. Abst. in C. A. 43:1175 (1949).

693. Milas, Chem. Rev., 10, 295 (1932).

694. Mills and Hart, J. Dairy Sci., 28, 1-13 (1945).

695. Mima, Ann. Repts. Takeda Research Lab., 11, 45-50 (1952).

696. Minatoya, Ando and Sugino, J. Soc. Rubber Ind. Japan, 13, 333 (1940).

697. Mital, U. S. Patent 2,373,631. Abst. in C. A. 40:1024 (1946).

698. Mitchell, F. and Cramp, U. S. Patent 2,654,660. Abst. in C. A. 48: 1669 (1954).

699. Mitchell, H. S., Kay, Hartanov and Ramsbottom, U. S. Patent 2,462,760. Abst. in C. A. 43:3540 (1949).

700. _____ and Silker, J. Agr. Food Chem., 1, 1163-5 (1953).

701. Mitler and Lieber, U. S. Patent 2,493,987. Abst. in C. A. 44:10314 (1950).

702. Molinair, Olii minerali grassie saponi, colori vernici, 25, 70-2 (1948).

703. Moore and Bickford, J. Am. Oil Chemists' Soc., 29, 1-4 (1952).

704. _____ and Waters, J. Chem. Soc., 3211 (1953).

705. Moran, U. S. Patent 2,326,483. Abst. in C. A. 38:861 (1944).

706. _____, Meyer, Otto and Oberright, U. S. Patent 2,383,494. Abst. in C. A. 39:5465 (1945).

707. Morawetz, Ind. Eng. Chem., 41, 1442-7 (1949).

708. Morgan and Watts, U. S. Patent 2,457,063. Abst. in C. A. 43:1880 (1949).

709. Mori, Naito, Ozawa and Kembo, Eiyo to Shokuryo (J. Japan Soc. Food Nutrition), 4, 105-9 (1951).

710. _____, _____, _____ and _____, Eiyô to Shokuryô (J. Japan Soc. Food Nutrition), 5, 180-2 (1952-53).

711. Morikawa, J. Soc. Chem. Ind. Japan, 47, 645-7 (1944).

712. Moritaka, Japan Patent 3,747-8. Abst. in C. A. 47:1904 (1953).

713. Morris, J. R., U. S. Patent 2,417,562. Abst. in C. A. 41:3613 (1947).

714. _____ and McCleary, U. S. Patent 2,374,559. Abst. in C. A. 40: 2292 (1946).

715. _____ and _____, U. S. Patent 2,409,303. Abst. in C. A. 41: 1427 (1947).

716. Morris, R. C., U. S. Patent 2,439,345. Abst. in C. A. 42:5054 (1948).

717. _____ and Horowitz, U. S. Patent 2,469,838. Abst. in C. A. 43: 6668 (1949).

718. _____ and Shokal, Brit. Patent 566,930. Abst. in C. A. 41:1711 (1947).

719. _____ and Van Winkle, U. S. Patent 2,465,912. Abst. in C. A. 43: 5185 (1949).

720. _____ and _____, U. S. Patent 2,494,515. Abst. in C. A. 44: 3032 (1950).

721. _____, _____ and Snider, U. S. Patent 2,542,286. Abst. in C. A. 45:4487 (1951).

722. Morris, S. G., Kraekel, Hammer, Myers and Riemenschneider, J. Am. Oil Chemists' Soc., 24, 309-11 (1947).

723. _____, Meyers, Kip, and Riemenschneider, J. Am. Oil Chemists' Soc., 27, 105-7 (1950).

724. _____ and Riemenschneider, J. Am. Oil Chemists' Soc., 26, 638-40 (1949).

725. _____ and _____, U. S. Patent 2,483,099. Abst. in C. A. 44: 2027 (1950).

726. Mosher, Conf. on Biol. Antioxidants, Trans. 4, 13-44 (1949); J. Franklin Inst., 251, 665-74 (1951).

727. Moureau and Dufraisse, Chem. Revs., 3, 113-62 (1926).

728. Mueller, J. Dairy Sci., 37, 754-60 (1954).

729. Muirhead, Oberweger, Seymour and Simmonite, J. Pharm. Pharmacol., 1, 762-73 (1949).

730. Mukherjee and Goswami, J. Indian Chem. Soc., 24, 239-48 (1947).

731. _____, Ray and Goswami, J. Indian Chem. Soc., 27, 539-44 (1950).

732. Murata, J. Soc. Rubber Ind. Japan, 22, 42-3 (1949).

733. _____, Ouchi and Noda, J. Soc. Rubber Ind. Japan, 22, 39-41 (1949).

734. Murphy, Ravner and Smith, Ind. Eng. Chem., 42, 2479-89 (1950).

735. Musco and Cruess, J. Agr. Food Chem., 2, 520-3 (1954).

736. Muset and Garcia-Valdecasas, Tabajos inst. nacl. cienc. méd., 2, 725-41 (1943-44).

737. Musher, U. S. Patent 2,342,162. Abst. in C. A. 38:4716 (1944).

738. _____, U. S. Patent 2,355,097-8. Abst. in C. A. 38:6420 (1944).

739. Musselman, U. S. Patent 2,413,332. Abst. in C. A. 41:1428 (1947).

740. Nagata and Kojima, Vitamins (Japan), 5, 206 (1952).

741. Nagy, Beadle and Kraybill, Oil & Soap, 22, 123-4 (1945).

742. _____, Vibrans and Kraybill, Oil & Soap, 21, 349-52 (1944).

743. Nair and Ramakrishnan, Bull. Central Research Inst. Univ. Travancore, Trivandrum Ser. A, 1, 30-4 (1950).

744. _____ and _____, Bull. Central Research Inst. Univ. Travancore, Ser. A, Phys. Sci., 2, 86-102 (1952).

745. _____ and _____, Current Sci., 13, 232 (1944).

746. Naito and Tsuchiya, J. Nippon Oil Technol. Soc., 3, No. 1/2, 134-40 (1950).

747. Nakanishi and Adachi, Tohoku J. Agr. Research, 3, 271-6 (1953).

748. _____, Kuroda, Kawanami and Adachi, Tohoku J. Agr. Research, 3, 113-25 (1952).

749. National Oil Products Co., Brit. Patent 589,273. Abst. in C. A. 41: 6740 (1947).

750. Neal, Gooding and Valterich, U. S. Patent 2,485,631-2. Abst. in C. A. 44:1728 (1950).

751. _____ and Vincent, U. S. Patent 2,370,987. Abst. in C. A. 39: 4256 (1945).

752. Nederlandsche Organisatie voor Toegepast-Natuurusten-schappelijk Onderzoek ten behoeve van de Voeding, Dutch Patent 66,584. Abst. in C. A. 45:5338 (1951).

753. Neely and Kavanagh, U. S. Patent 2,367,470. Abst. in C. A. 39:5469 (1945).

754. Nelson, U. S. Patent 2,342,887. Abst. in C. A. 38:5078 (1944).

755. _____, U. S. Patent 2,612,488. Abst. in C. A. 47:1969 (1953).

756. Neumer and Dugan, Food Technol., 7, 189-91 (1953).

757. Newby, U. S. Patent 2,549,118. Abst. in C. A. 45:5964 (1951).

758. _____, U. S. Patent 2,628,953. Abst. in C. A. 47:4644 (1953).

759. _____, U. S. Patent 2,660,605. Abst. in C. A. 48:2405 (1954).

760. Nishida, Yamamoto, Kobayashi and Yamamoto, Mem. Fac. Agr. Kagoshima Univ., 1, 75-86 (1952).

761. Nobori, J. Soc. Chem. Ind. Japan, 46, 15-17 (1943).

762. Nogami, Matsuda and Nagasawa, J. Pharm. Soc. Japan, 71, 813-17 (1951).

763. Norris, U. S. Patent 2,377,029-31. Abst. in C. A. 39:3449 (1945).

764. _____, U. S. Patent 2,462,663-4. Abst. in C. A. 43:3540 (1949).

765. Nyrop, Brit. Patent 640,241. Abst. in C. A. 44:9587 (1950).

766. _____, Dan. Patent 71,108. Abst. in C. A. 45:372 (1951).

767. Oberright, U. S. Patent 2,458,526-7. Abst. in C. A. 43:2766 (1949).

768. _____, U. S. Patent 2,459,112-16. Abst. in C. A. 43:2766 (1949).

769. _____, U. S. Patent 2,542,831. Abst. in C. A. 45:4032 (1951).

770. _____, U. S. Patent 2,542,832. Abst. in C. A. 45:10569 (1951).

771. _____, U. S. Patent 2,589,326. Abst. in C. A. 46:11227 (1952).

772. Oesterreichisch-Amerikanische Gummiwerke A.-G., Austrian Patent 162,865. Abst. in C. A. 46:4840 (1952).

773. Ohlmann and Thurbar, U. S. Patent 2,665,312. Abst. in C. A. 48:4213 (1954).

774. Ohshima, Japan Patent 3,829. Abst. in C. A. 48:9086 (1954).

775. Olcott, J. Am. Chem. Soc., 56, 2492 (1934).

776. _____ and Campbell, U. S. Patent 2,652,332. Abst. in C. A. 48: 1033 (1954).

777. _____ and Emerson, J. Am. Chem. Soc., 59, 1008-9 (1937).

778. O'Leary, U. S. Patent 2,397,976. Abst. in C. A. 40:3626 (1946).

779. Oliver, Singleton and Bailey, Oil & Soap, 21, 188-93 (1944).

780. Olsen, Iva, 19, 149-63 (1948); Abst. in Sugar Ind. Abstracts, 10, No. 11, 130 (1948).

781. Ono and Toyama, J. Chem. Soc. Japan, 65, 611-15 (1944).

782. Oosterhout and Roddy, U. S. Patent 2,621,147. Abst. in C. A. 47: 4594 (1953).

783. OPCO Chemical Co., Brit. Patent 591,511. Abst. in C. A. 42:3978 (1948).

784. Orten, Kuyper and Smith, Food Technol., 2, 308-16 (1948).

785. Oshima, Yoshihara and Arima, J. Agr. Chem. Soc. Japan, 25, 344-6 (1951-52).

786. _____, _____, Nagamizu and Arima, J. Agr. Chem. Soc. Japan, 25, 53-5 (1951-52).

787. Osterhof, U. S. Patent 2,381,180. Abst. in C. A. 39:5116 (1945).

788. Otto, U. S. Patent 2,387,286. Abst. in C. A. 40:5562 (1946).

789. _____, U. S. Patent 2,403,453. Abst. in C. A. 40:5915 (1946).

790. _____ and Meyer, U. S. Patent 2,383,497. Abst. in C. A. 40:721 (1946).

791. _____ and _____, U. S. Patent 2,483,736. Abst. in C. A. 44: 1692 (1950).

792. Overman, Food Research, 16, 39-42 (1951).

793. Owen, U. S. Patent 2,401,658. Abst. in C. A. 40:6098 (1946).

794. Paquot, Inds. corps gras, 3, 111-17, 140-3 (1947).

795. Patel and Sreenivasan, J. Sci. Ind. Research (India), 9B, No. 4, 99-102 (1950).

796. Patterson, J. A., U. S. Patent 2,363,896. Abst. in C. A. 39:3926 (1945).

797. _____ and McCleary, U. S. Patent 2,388,074. Abst. in C. A. 40: 721 (1946).

798. Patterson, W. I. and Williamson, U. S. Patent 2,455,088. Abst. in C. A. 43:1586 (1949).

799. Paul, U. S. Patent 2,348,842. Abst. in C. A. 39:1567 (1945).

800. _____, U. S. Patent 2,349,749. Abst. in C. A. 39:1318 (1945).

801. _____, U. S. Patent 2,363,687. Abst. in C. A. 39:3176 (1945).

802. _____, U. S. Patent 2,373,335. Abst. in C. A. 40:1056 (1946).

803. _____, U. S. Patent 2,381,771. Abst. in C. A. 40:2030 (1946).

804. _____ and Hunter, U. S. Patent 2,421,352. Abst. in C. A. 41:5337 (1947).

805. Pavlyuchenko and Sokolove, Zhur. Priklad Khim (J. Applied Chem.), 21, 1168-73 (1948).

806. Pearl, U. S. Patent 2,644,822. Abst. in C. A. 48:6468 (1954).

807. Pedersen, Ind. Eng. Chem., 41, 924-8 (1949).

808. _____, U. S. Patent 2,382,904. Abst. in C. A. 39:5472 (1945).

809. _____, U. S. Patent 2,443,835. Abst. in C. A. 43:1794 (1949).

810. _____ and Bender, U. S. Patent 2,382,905-6. Abst. in C. A. 39: 5475 (1945).

811. _____ and _____, U. S. Patent 2,401,957. Abst. in C. A. 40: 6797 (1946).

812. _____ and Downing, U. S. Patent 2,462,668. Abst. in C. A. 43: 4687 (1949).

813. Penn, U. S. Patent 2,444,307. Abst. in C. A. 42:6472 (1948).

814. Pérez de Paladino, Rev. farm. (Buenos Aires), 94, 212-16 (1952).

815. Perry and Talley, U. S. Patent 2,621,159. Abst. in C. A. 47:2973 (1953).

816. Petering and Petering, U. S. Patent 2,482,635. Abst. in C. A. 44: 246 (1950).

817. Phelpot and Black, U. S. Patent 2,374,234. Abst. in C. A. 39:3450 (1945).

818. Piccard, Ber., 46, 1853 (1913).

819. Pinazzi and Billuart, Rev. gén. caoutchouc, 31, 123-31 (1954).

820. Piskur, Oil & Soap, 22, 84-100 (1945).

821. _____ and Higgins, U. S. Patent 2,461,081. Abst. in C. A. 43: 3948 (1949).

822. Polister and Mead, J. Agr. Food Chem., 2, 199-202 (1954).

823. Popper, Steigmann and Dyniewicz, Gastroenterology, 10, 987-1000 (1948).

824. Powers and Fellers, J. Home Econ., 37, 294-6 (1945).

825. Pratt, U. S. Patent 2,472,437. Abst. in C. A. 43:6665 (1949).

826. Privett and Quackenbush, J. Am. Oil Chemists' Soc., 31, 169-71, 281-3 (1954).

827. Prutton, Smith and Frey, U. S. Patent 2,365,291. Abst. in C. A. 39:4752 (1945).

828. Pyenson and Tracy, J. Dairy Sci., 31, 539-50 (1948).

829. _____ and _____, J. Dairy Sci., 33, 815-19 (1950).

830. Raasch, U. S. Patent 2,612,500. Abst. in C. A. 47:3736 (1953).

831. Rac, Kem. Viestnik, 15-16, 67-75 (in Ger. 75-6) (1941-42).

832. Raeithel, Z. Lebensm.-Unterauch. u.-Forsch, 95, 246-62 (1952).

833. Ramaswamy and Banerjee, Ann. Biochem. and Exptl. Med., 8, 55-68, 115-22 (1948).

834. Ramon and Richon, Presse méd., 55, 693-4 (1947).

835. Raw, Science, 118, 159-60 (1953).

836. Rawlins, Holcomb, Jones, Tendick and Burckhalter, U. S. Patent 2,459,338. Abst. in C. A. 43:4695 (1949).

837. Reder, Science, 103, 201-3 (1946).

838. Reiff, U. S. Patent 2,326,496. Abst. in C. A. 38:861 (1944).

839. _____, U. S. Patent 2,366,873. Abst. in C. A. 39:3154 (1945).

840. _____, U. S. Patent 2,381,854. Abst. in C. A. 39:5472 (1945).

841. _____ and Andress, U. S. Patent 2,438,876. Abst. in C. A. 42: 5657 (1948).

842. _____ and _____, U. S. Patent 2,528,782. Abst. in C. A. 45: 2194 (1951).

843. _____ and Andrus, U. S. Patent 2,401,273. Abst. in C. A. 40: 5238 (1946).

844. _____ and Hartough, U. S. Patent 2,367,377. Abst. in C. A. 39: 3426 (1945).

845. _____ and _____, U. S. Patent 2,462,426. Abst. in C. A. 43: 4457 (1949).

846. Reimers, Arch. Pharm. Chemi, 50, 159-65 Chem. Zentr. 1943, II, 544-5.

847. _____, Quart. J. Pharm. Pharmacol., 19, 172-87 (1946).

848. Reinart, Proc. 12th Intern. Dairy Congr., 2, 405-15 (1949).

849. Reith, Conserva, 2, 133-6 (1953).

850. Rescigno, Lalte, 25, 292-300 (1951).

851. Revukas, U. S. Patent 2,570,377. Abst. in C. A. 46:725 (1952).

852. Ribeiro and Cardoso, Rev. faculdade med. vet. Univ. Sao Paulo, 4, 235-40 (1950).

853. Richards, U. S. Patent 2,402,448. Abst. in C. A. 40:6808 (1946).

854. Richardson, El-Rafey and Long, J. Dairy Sci., 30, 397-413 (1947).

855. Richter and Fuller, U. S. Patent 2,479,513. Abst. in C. A. 43:9432 (1949).

856. Riemenschneider, Trans. Am. Assoc. Cereal Chemists, 5, 50-63 (1947).

857. _____ and Ault, Food Industries, 16, No. 11, 78-80, 122-25 (1944).

858. _____, Herb, Hammaker and Luddy, Oil & Soap, 21, 307-9 (1944).

859. _____ and Turer, U. S. Patent 2,375,250. Abst. in C. A. 39:3449 (1945).

860. _____ and _____, U. S. Patent 2,383,815-16. Abst. in C. A. 39:5517 (1945).

861. _____ and _____, U. S. Patent 2,440,383. Abst. in C. A. 42: 5694 (1948).

862. _____, _____ and Ault, Oil & Soap, 21, 98-100 (1944).

863. _____, _____, Wells and Ault, Oil & Soap, 21, 47-50 (1944).

864. Rigby, U. S. Patent 2,582,395. Abst. in C. A. 46:10553 (1952).

865. Ris, Ber., 19, 2206 (1886).

866. Ritter, J. Am. Chem. Soc., 69, 46-50 (1947).

867. Rittschof and Proell, U. S. Patent 2,392,881. Abst. in C. A. 40: 2030 (1946).

868. Rhines, U. S. Patent 2,560,743. Abst. in C. A. 45:9298 (1951).

869. Roberts, U. S. Patent 2,463,429. Abst. in C. A. 43:4007 (1949).

870. Robey and Barnett, U. S. Patent 2,445,367. Abst. in C. A. 42:8207 (1948).

871. _____, Fedirks and Barnett, U. S. Patent 2,449,010. Abst. in C. A. 43:386 (1949).

872. Robinson, Food Technol., 5, 20-46 (1951).

873. Robison, U. S. Patent 2,645,581. Abst. in C. A. 47:10150 (1953).

874. Roemer and Kaiser, U. S. Patent 2,650,220. Abst. in C. A. 48:9412 (1954).

875. Rogers and McNab, U. S. Patent 2,447,619. Abst. in C. A. 42:7976 (1948).

876. _____ and _____, U. S. Patent 2,562,506. Abst. in C. A. 45: 2195 (1951).

877. Roine, Acta. Chem. Soand., 2, 97-108 (1948).

878. Rosenwald, U. S. Patent 2,459,540. Abst. in C. A. 43:3187 (1949).

879. _____, U. S. Patent 2,555,509. Abst. in C. A. 45:8276 (1951).

880. _____, U. S. Patent 2,616,931. Abst. in C. A. 48:722 (1954).

881. _____, U. S. Patent 2,679,459. Abst. in C. A. 48:9674 (1954).

882. _____ and Chenicek, J. Am. Oil Chemists' Soc., 28, 185 (1951).

883. _____ and _____, U. S. Patent 2,666,709. Abst. in C. A. 48: 6049 (1954).

884. _____ and Hoatson, Ind. Eng. Chem., 41, 914-18 (1949).

885. _____, _____ and Chenicek, Ind. Eng. Chem., 42, 162-5 (1950).

886. Ross, Backoff and Williams, U. S. Patent 2,371,319. Abst. in C. A. 40:731 (1946).

887. _____, Bartlett and Hard, Food Technol., 7, 153-6 (1953).

888. Rothrock and Conyne, U. S. Patent 2,437,232. Abst. in C. A. 42: 4399 (1948).

889. Roy, Indian Soap J., 11, 203-9 (1946).

890. Rudel, U. S. Patent 2,662,815. Abst. in C. A. 48:3023 (1954).

891. _____ and Boyle, U. S. Patent 2,523,146. Abst. in C. A. 45:1157 (1951).

892. Ruggles, U. S. Patent 2,443,569. Abst. in C. A. 42:6107 (1948).

893. Rusch, Biol. Antioxidants, Trans. 2nd Conf. 1947, 106-16.

894. Russoff, U. S. Patent 2,657,997. Abst. in C. A. 48:2286 (1954).

895. Rust, U. S. Patent 2,447,876. Abst. in C. A. 42:8484 (1948).

896. Rutkowski, Roczniki Państwowego Zakladu Hig., 3, 71-88 (1952).

897. Sabalitschka, Österr Apoth Ztg., 3, 458-67 (1949).

898. _____ and Boehm, U. S. Patent 2,255,191. Abst. in C. A. 36:289 (1942).

899. Sabato, Bol. inform. petrol., 27, No. 301, 59-67 (1950).

900. Sahasrabudhe, J. Sci. Ind. Research, 12B, 63-7 (1953).

901. Sakurai and Tanabe, Yakugaku (Science of Drugs), 1, 88-90 (1947).

902. Salomone, Olearia, 1947, 31-3.

903. Sandell, Farm. Revy., 45, 697-711 (1946).

904. _____, Svensk Farm. Tid., 54, 473-91, 501-13, 525-33 (1950).

905. _____ and Spross, Svensk Farm. Tid., 54, 61-73 (1950).

906. Sarger, Chem.-Ztg., 67, 344-7 (1943).

907. Saunders and Murphy, U. S. Patent 2,609,343. Abst. in C. A. 47:856 (1953).

908. Scanley, U. S. Patent 2,619,465. Abst. in C. A. 47:2480 (1953).

909. Scheiber, Farbe u. Lack, 1947, 29-31, 50-2.

910. Schillak, Przemysl Rolny i Spoz, 4, 296-302 (1950).

911. Schmerling and Chenicek, U. S. Patent 2,573,933. Abst. in C. A. 46: 2282 (1952).

912. Schmidt-Nielsen and Naerland, Kgl. Norske Videnskab Selskab., Forh., 16, 157-60 (1943).

913. Schreiber, U. S. Patent 2,370,080. Abst. in C. A. 39:5470 (1945).

914. Schuler and Meier, Helv. Physiol. Pharmacol. Acta, 2, 83-5 (1944).

915. Schulte and Schillinger, Z. Lebensm.-Untersuch. u-Forsch., 94, 166-82 (1952).

916. Schulz, Strassberger and Glindemann, Makromol. Chem., 1, 94-105 (1947).

917. Schwab and Dutton, U. S. Patent 2,636,887. Abst. in C. A. 47:7242 (1953).

918. Schweitzer, U. S. Patent 2,416,068. Abst. in C. A. 41:3483 (1947).

919. Schwenk and Henderson, U. S. Patent 2,376,884. Abst. in C. A. 39: 3883 (1945).

920. _____ and _____, U. S. Patent 2,377,188. Abst. in C. A. 39: 3634 (1945).

921. Scott, U. S. Patent 2,353,591-2. Abst. in C. A. 38:6130 (1944).

922. _____, U. S. Patent 2,379,460. Abst. in C. A. 39:4257 (1945).

923. _____, U. S. Patent 2,456,154. Abst. in C. A. 43:3650 (1949).

924. Seubert and Andrews, Modern Packaging, 26, No. 4, 153-4 (1952).

925. _____ and _____, Tappi, 36, No. 6, 174A-5A (1953).

926. Seyfried, U. S. Patent 2,434,522. Abst. in C. A. 42:2422 (1948).

927. Shappirio, U. S. Patent 2,338,207. Abst. in C. A. 38:3744 (1944).

928. _____, U. S. Patent 2,352,229. Abst. in C. A. 38:5682 (1944).

929. _____, U. S. Patent 2,430,031. Abst. in C. A. 42:1752 (1948).

930. _____, U. S. Patent 2,458,535. Abst. in C. A. 43:3193 (1949).

931. _____, U. S. Patent 2,536,100. Abst. in C. A. 45:3175 (1951).

932. _____, U. S. Patent 2,587,581. Abst. in C. A. 46:5308 (1952).

933. Shelton and Cox, Ind. Eng. Chem., 45, 386-92 (1953).

934. _____ and _____, Ind. Eng. Chem., 46, 816-23 (1954).

935. Shipner, U. S. Patent 2,457,741. Abst. in C. A. 43:2793 (1949).

936. Shishido and Kuyama, Bull. Inst. Chem. Research, Kyoto Univ., 25, 73-4 (1951).

937. _____ and _____, Bull. Inst. Chem. Research, Kyoto Univ., 26, 87-8 (1951).

938. _____ and _____, Bull. Inst. Chem. Research, Kyoto Univ., 30, 49-50 (1952).

939. Shtal'berg, Molochnaya Prom., 10, No. 8, 7-8 (1949).

940. Sibley, U. S. Patent 2,325,152. Abst. in C. A. 38:510 (1944).

941. _____, U. S. Patent 2,335,089. Abst. in C. A. 38:2849 (1944).

942. _____, U. S. Patent 2,370,756. Abst. in C. A. 39:4095 (1945).

943. Sievers, Annual report for the fiscal year ending June 30, 1945. Mass. Agr. Expt. Sta. Bull. 428 (1945).

944. Silver, Food Industries, 17, 1454-6, 1596, 1598, 1600 (1945).

945. Simamura and Hamashima, Bull. Chem. Soc. Japan, 25, 358-9 (1952).

946. Simons and Buxton, U. S. Patent 2,331,432. Abst. in C. A. 38:1610 (1944).

947. Sisley, Rev. fermentations et inds. aliment., 5, 126-35 (1950).

948. Sjöström, Svenska Mejeritidningen, 44, 152-60 (1952).

949. _____ and Larsson, Proc. 12th Intern. Dairy Congr., 2, 368-74 (1949).

950. Sloan, U. S. Patent 2,379,936. Abst. in C. A. 39:4256 (1945).

951. _____, U. S. Patent 2,419,735. Abst. in C. A. 41:4664 (1947).

952. _____, U. S. Patent 2,419,736. Abst. in C. A. 41:4811 (1947).

953. Small and Ubbelohde, J. Chem. Soc., 1953, 637-42.

954. Smith, A. I., U. S. Patent 2,456,569. Abst. in C. A. 43:3193 (1949).

955. Smith, F. G. and Stotz, The action of copper and antioxidant in linoleic acid autoxidation. N. Y. Agr. Expt. Sta., Tech. Bull. 276 (1946).

956. Smith, F. H., Brady and Comstock, Ind. Eng. Chem., 37, 1206-9 (1945).

957. Smith, G. E. P, U. S. Patent 2,514,199. Abst. in C. A. 44:9720 (1950).

958. _____, U. S. Patent 2,581,906. Abst. in C. A. 46:3791 (1952).

959. _____, U. S. Patent 2,581,940. Abst. in C. A. 46:3317 (1952).

960. _____ and Albert, U. S. Patent 2,581,924. Abst. in C. A. 46: 4837 (1952).

961. Smith, H. G. and Cantrell, U. S. Patent 2,397,702. Abst. in C. A. 40:3891 (1946).

962. _____ and _____, U. S. Patent 2,522,312. Abst. in C. A. 44: 11083 (1950).

963. _____ and _____, U. S. Patent 2,528,092. Abst. in C. A. 45: 1338 (1951).

964. _____, _____ and Hill, U. S. Patent 2,602,049. Abst. in C. A. 47:302 (1953).

965. _____, _____ and Peters, U. S. Patent 2,454,890. Abst. in C. A. 43:2424 (1949).

966. _____, _____ and _____, U. S. Patent 2,504,742-3. Abst. in C. A. 44:5576 (1950).

967. _____, _____ and _____, U. S. Patent 2,511,744. Abst. in C. A. 44:9145 (1950).

968. _____, _____ and _____, U. S. Patent 2,513,061. Abst. in C. A. 44:9666 (1950).

969. _____, _____ and _____, U. S. Patent 2,516,654. Abst. in C. A. 45:855 (1951).

970. _____, _____ and _____, U. S. Patent 2,527,279. Abst. in C. A. 45:344 (1951).

971. _____, _____ and _____, U. S. Patent 2,545,113-14. Abst. in C. A. 45:7786 (1951).

972. _____, _____ and _____, U. S. Patent 2,656,259-60. Abst. in C. A. 48:1668 (1954).

973. Smith, L. I. and Unguade, U. S. Patent 2,411,942. Abst. in C. A. 41: 2447 (1947).

974. Smith, N. L., J. Org. Chem., 16, 415-18 (1951).

975. _____, U. S. Patent 2,572,066. Abst. in C. A. 46:3570 (1952).

976. _____, U. S. Patent 2,587,660-2. Abst. in C. A. 46:9128 (1952).

977. Snyder and Fuller, U. S. Patent 2,364,030. Abst. in C. A. 39:3911 (1945).

978. Société civile d'études d'appareillages et d'equipements pour fluides, Fr. Patent 947,990. Abst. in C. A. 45:4086 (1946).

979. Société Internationale d'éditions, Fr. Patent 863,604. Abst. in C. A. 42:9198 (1948).

980. Soday, U. S. Patent 2,462,684. Abst. in C. A. 43:4511 (1949).

981. Somogyi, Helv. Physiol. Pharmacol. Acta, 3, C15-16 (1945).

982. Spetsig, Svensk Kem. Tid., 64, 191-5 (1952).

983. _____, Svensk Kem. Tid., 65, 65-9 (1953).

984. Spicer, U. S. Patent 2,567,131. Abst. in C. A. 46:2565 (1952).

985. Standard Oil Development Co., Brit. Patent 577,955. Abst. in C. A. 41:1836 (1947).

986. _____, Brit. Patent 580,845. Abst. in C. A. 41:1586 (1947).

987. _____, Brit. Patent 581,747. Abst. in C. A. 41:2571 (1947).

988. _____, Brit. Patent 581,783. Abst. in C. A. 41:2571 (1947).

989. _____, Brit. Patent 586,333. Abst. in C. A. 41:6709 (1947).

990. _____, Brit. Patent 590,885. Abst. in C. A. 42:752 (1948).

991. _____, Brit. Patent 591,717. Abst. in C. A. 42:752 (1948).

992. _____, Brit. Patent 592,924. Abst. in C. A. 42:2423 (1948).

993. _____, Brit. Patent 652,683. Abst. in C. A. 45:8758 (1951).

994. _____, Fr. Patent 942,798. Abst. in C. A. 45:1339 (1951).

995. Stanistreet and Byrne, Australasian J. Pharm., 27, 730-3 (1946).

996. Stanley, Colloid Chemistry, 6, 263-7 (1946).

997. Stefl and Bentz, U. S. Patent 2,514,216. Abst. in C. A. 44:9725 (1950).

998. Sterman, U. S. Patent 2,585,182. Abst. in C. A. 46:4216 (1952).

999. Stern, Robeson, Weisler and Baxter, J. Am. Chem. Soc., 69, 869-74 (1947).

1000. Stevens and Dubbs, U. S. Patent 2,515,906-7. Abst. in C. A. 44:9481 (1950).

1001. _____ and _____, U. S. Patent 2,515,908. Abst. in C. A. 44: 9666 (1950).

1002. _____ and _____, U. S. Patent 2,515,909. Abst. in C. A. 44: 9483 (1950).

1003. _____ and _____, U. S. Patent 2,570,402. Abst. in C. A. 46: 725 (1952).

1004. _____ and Starnes, U. S. Patent 2,535,705. Abst. in C. A. 45: 2193 (1951).

1005. Stewart, U. S. Patent 2,577,719. Abst. in C. A. 46:2795 (1952).

1006. _____ and Clayton, U. S. Patent 2,543,074. Abst. in C. A. 45: 5399 (1951).

1007. _____ and _____, U. S. Patent 2,543,734. Abst. in C. A. 45: 4033 (1951).

1008. Stillson, U. S. Patent 2,428,745. Abst. in C. A. 42:354 (1948).

1009. _____ and Sawyer, U. S. Patent 2,459,597. Abst. in C. A. 43: 3459 (1949).

1010. Stirton, Turer and Riemenschneider, Oil & Soap, 22, 81-3 (1945).

1011. Stoloff, Puncohar and Crowther, Food Inds., 20, 1130-2, 1258 (1948).

1012. Storgards, Proc. 12th Intern. Dairy Cong., 2, 235-7 (1949).

1013. Strachan and Moyls, Food Technol., 3, 327-32 (1949).

1014. Strel'tsova, Trudy Moskov. Khim.-Tekh. Inst. Mendeleeva, 1940, No. 6, 103-11; Khim. Referat. Zhur., 4, No. 9, 123 (1941).

1015. Strickland, Anal. Chem., 20, 55-6 (1948).

1016. _____, U. S. Patent 2,606,476. Abst. in C. A. 47:854 (1953).

1017. Stull, Herreid and Tracy, J. Dairy Sci., 32, 301-5 (1949).

1018. _____, _____ and _____, J. Dairy Sci., 34, 181-94 (1951).

1019. Suzuki, Nagata, Takata and Katsui, Vitamins (Japan), 5, 337-42 (1952).

1020. Swartling, Proc. 12th Intern. Dairy Congr., 2, 375-81 (1949).

1021. _____ and Samuelsson, Svenska Mejeritidn., 45, 215-18 (1953).

1022. Swenson, Miers, Schultz and Owens, Food Technol., 7, 232-35 (1953).

1023. Swern, Stirton, Turer and Wells, Oil & Soap, 20, 224-6 (1943).

1024. Swift, Mann and Fisher, Oil & Soap, 21, 317 (1944).

1025. Takata and Nagata, Vitamins (Japan), 5, 203-5 (1952).

1026. _____ and Shimizu, Vitamins (Japan), 5, 126-8 (1952).

1027. Tamura, Ohkuma and Hayashi, J. Agr. Chem. Soc. Japan, 26, 410-12 (1952).

1028. Tappel, Arch. Biochem. Biophys., 47, 223-5 (1953).

1029. _____, Lundberg and Boyer, Arch. Biochem. Biophys., 42, 293-304 (1953).

1030. Tarassuk and Henderson, J. Dairy Sci., 25, 774-5 (1942).

1031. Tarr, Fisheries Research Board Can., Progress Repts. Pacific Coast Stas. No. 64, 57-61 (1945).

1032. _____, J. Fisheries Research Board Can., 7, 137-54 (1947).

1033. _____, J. Fisheries Research Board Can., 7, 237-47 (1948).

1034. _____ and Cooke, J. Fisheries Research Board Can., 7, 522-7 (1949).

1035. Taub and Simone, U. S. Patent 2,432,698. Abst. in C. A. 42:2130 (1948).

1036. Täufel and Arens, Fette u. Seifen, 51, 131-3, 307-9 (1944).

1037. _____ and Müller, Biochem. Z., 315, 381-90 (1943).

1038. _____ and Rothe, Angew. Chem., 61, 84-9 (1949).

1039. _____ and _____, Fette u. Seifen, 50, 434-7 (1943).

1040. _____ and _____, Fette u. Seifen, 51, 100-02 (1944).

1041. _____ and _____, Fette u. Seifen, 53, 381-5 (1951).

1042. Taylor, A. W. C., Brit. Patent 655,991. Abst. in C. A. 46:7592 (1952).

1043. Taylor, H. S., Biol. Antioxidants, Trans. 1st Conf., 1946, 5-15.

1044. _____, Biol. Antioxidants, Trans. 2nd Conf., 1947, 9-12.

1045. Teeter, U. S. Patent 2,621,172. Abst. in C. A. 47:3556 (1953).

1046. Ter Horst, Can. Patent 421,523. Abst. in C. A. 38:5098 (1944).

1047. Terrier and Deshusses, Mitt. Lebensm. Hyg., 40, 221-6 (1949).

1048. Thaler and Schottmayer, Fette u. Seifen, 49, 646-52 (1942).

1049. Thiele and Heuser, Ann., 290, 31 (1896).

1050. Thome, Olsson, Lodin and Buhrgard, Medd. Statens Mezeriförsök, 32, 21 pp. (1951).

1051. Thompson, Ind. Eng. Chem., 43, 1638-41 (1951).

1052. _____, U. S. Patent 2,251,425. Abst. in C. A. 44:11084 (1950).

1053. _____, U. S. Patent 2,492,334. Abst. in C. A. 44:5496 (1950).

1054. _____, U. S. Patent 2,498,630. Abst. in C. A. 44:4240 (1950).

1055. _____, U. S. Patent 2,542,972. Abst. in C. A. 45:4919 (1951).

1056. _____, U. S. Patent 2,633,425. Abst. in C. A. 48:2114 (1954).

1057. _____, U. S. Patent 2,648,691. Abst. in C. A. 47:11763 (1953).

1058. _____, U. S. Patent 2,677,617. Abst. in C. A. 48:10332 (1954).

1059. _____ and Chenicek, U. S. Patent 2,462,237. Abst. in C. A. 43: 3604 (1949).

1060. _____, _____ and Symon, Ind. Eng. Chem., 44, 1659-62 (1952).

1061. Tilicheev, Lesnaya Prom., 1, No. 2, 27-3 (1941).

1062. _____, Volf and Kaminer, Lesnaya Prom., 1941, No. 4, 28-35; Chem. Zentr. 1943, I, 1438.

1063. Tillitson, U. S. Patent 2,472,868. Abst. in C. A. 43:7647 (1949).

1064. Titaev, Biokhimiya, 13, 197-206 (1948).

1065. Tollenaar, Centraal Inst. Voedingsonderzoek T.N.O., Utrecht, Publ. No. 148, 16 pp. (1953).

1066. _____, Centraal Inst. Voedingsonderzoek, T.N.O., Utrecht, Publ. No. 166, 148 pp. (1953).

1067. _____, Conserva, 2, 304-7 (1954).

1068. _____, Dutch Patent 71,606. Abst. in C. A. 47:9522 (1953).

1069. _____, Olearia, 7, 5-14 (1953).

1070. _____, Proc. 12th Intern. Dairy Cong., 2, 357-67 (1949).

1071. _____, U. S. Patent 2,502,109. Abst. in C. A. 44:5495 (1950).

1072. _____, U. S. Patent 2,586,274. Abst. in C. A. 46:4124 (1952).

1073. _____ and Mossel, Proc. 13th Intern. Dairy Cong., 3, 1381-8 (1953).

1074. Tom, U. S. Patent 2,506,847. Abst. in C. A. 44:7525 (1950).

1075. Trenner, U. S. Patent 2,483,251. Abst. in C. A. 44:3521 (1950).

1076. Tressler and DuBois, Food Industries, 16, No. 9, 75, 137-39 (1944).

1077. Trueger and Sprague, U. S. Patent 2,422,321. Abst. in C. A. 41:5712 (1947).

1078. Tulagin, U. S. Patent 2,414,491. Abst. in C. A. 41:3387 (1947).

1079. Ulex and Kroger, Deut. Lebensm. Rundschau, 46, 256-60 (1951).

1080. U. S. Rubber Co., Brit. Patent 557,752. Abst. in C. A. 39:3460 (1945).

1081. _____, Brit. Patent 560,958. Abst. in C. A. 40:3929 (1946).

1082. _____, Brit. Patent 570,045. Abst. in C. A. 40:4554 (1946).

1083. _____, Brit. Patent 570,232. Abst. in C. A. 40:5596 (1946).

1084. _____, Brit. Patent 571,813. Abst. in C. A. 41:4328 (1947).

1085. _____, Brit. Patent 578,966. Abst. in C. A. 44:11157 (1950).

1086. _____, Brit. Patent 687,833. Abst. in C. A. 47:7812 (1953).

1087. Univ. of Minn., Brit. Patent 618,406. Abst. in C. A. 43:5157 (1949).

1088. Urry and Eiszner, J. Am. Chem. Soc., 74, 5822-6 (1952).

1089. Vahlteich, Neal and Gooding, U. S. Patent 2,523,792. Abst. in C. A. 45:374 (1951).

1090. Valentine, U. S. Patent 2,380,129-30. Abst. in C. A. 39:4516 (1945).

1091. _____, U. S. Patent 2,489,000. Abst. in C. A. 44:5917 (1950).

1092. Valpola, Teknillisen Kemian Aikakansilehti, 10, 461-2 (1953).

1093. van Battum, Dutch Patent 69,044. Abst. in C. A. 46:7758 (1952).

1094. Van Blaricour and Martin, Food Technol., 5, 337-9 (1951).

1095. van Melsen, Dutch Patent 59,015. Abst. in C. A. 41:5900 (1947).

1096. van Sluis, Food Manuf., 26, 91-101 (1951).

1097. Vas, Műegyetemi Közlemények, 1947, No. 1, 79-87.

1098. Vaughn and Bean, U. S. Patent 2,618,657. Abst. in C. A. 47:9359 (1953).

1099. Verberg and Weevers Stous, Dutch Patent 70,430. Abst. in C. A. 47: 856 (1953).

1100. Vitlar, Bol. inst. sudamericano petrol, 1, No. 2, 145-58 (1943).

1101. Vittum, U. S. Patent 2,384,658. Abst. in C. A. 39:5192 (1945).

1102. _____ and Wilder, Brit. Patent 560,371. Abst. in C. A. 40:1406 (1946).

1103. Vlieschauwer, Hendix and Walley, Proc. 13th Intern. Dairy Congr., 3, 1092-5 (1953).

1104. Von Bramer, U. S. Patent 2,487,909. Abst. in C. A. 44:2221 (1950).

1105. _____ and Ruggles, U. S. Patent 2,436,838. Abst. in C. A. 42: 3950 (1948).

1106. _____ and _____, U. S. Pat. Appl. 649,770 Official Gaz., 652, 1181 (1951).

1107. Voorthuis and van Dijk, Dutch Patent 70,853. Abst. in C. A. 47:5170 (1953).

1108. Vore, U. S. Patent 2,325,085. Abst. in C. A. 38:256 (1944).

1109. _____, U. S. Patent 2,325,167. Abst. in C. A. 38:488 (1944).

1110. Vrbaski, Arhiv Kem., 22, 101-15 (1950).

1111. Wachs, Biochem. Z., 319, 561-70 (1949).

1112. _____, Fette u. Seifen, 52, 466-70 (1950).

1113. Waitkins, U. S. Patent 2,506,049. Abst. in C. A. 44:6618 (1950).

1114. Walsh, Trans. Faraday Soc., 45, 1043-8 (1949).

1115. Walters, U. S. Patent 2,395,382. Abst. in C. A. 40:2972 (1946).

1116. _____, U. S. Patent 2,410,846. Abst. in C. A. 41:1091 (1947).

1117. _____ and Busso, Ind. Eng. Chem., 41, 907-14 (1949).

1118. Wasserman, U. S. Patent 2,586,191. Abst. in C. A. 46:4216 (1952).

1119. _____ and Caplan, U. S. Patent 2,571,091. Abst. in C. A. 46:725 (1952).

1120. Wasson and Smith, Ind. Eng. Chem., 45, 197-200 (1953).

1121. _____ and _____, U. S. Patent 2,362,516. Abst. in C. A. 39: 5450 (1945).

1122. _____ and Wilson, U. S. Patent 2,366,074. Abst. in C. A. 40:454 (1946).

1123. _____ and _____, U. S. Patent 2,438,468. Abst. in C. A. 42: 4341 (1948).

1124. Waters and Wickham-Jones, J. Chem. Soc., 1951, 812-23.

1125. Watson, U. S. Patent 2,451,642. Abst. in C. A. 43:1179 (1949).

1126. _____, U. S. Patent 2,463,836. Abst. in C. A. 43:4459 (1949).

1127. _____ and Gaynor, U. S. Patent 2,402,792. Abst. in C. A. 40:5238 (1946).

1128. _____ and Tom, Ind. Eng. Chem., 41, 918-23 (1949).

1129. Watts, J. Am. Oil Chemists' Soc., 27, 48-51 (1950).

1130. _____ and Wong, Arch. Biochem., 30, 110-20 (1951).

1131. Webber, U. S. Patent 2,599,794. Abst. in C. A. 46:8846 (1952).

1132. Weber, Arhiv Kem., 19, 1-8 (in Eng. 8-9) (1947).

1133. Weier and Stocking, J. Agr. Research, 78, 503-15 (1949).

1134. _____ and _____, Science, 104, 437-8 (1946).

1135. Weinstein and Trout, J. Dairy Sci., 34, 554-64 (1951).

1136. Weiss, U. S. Patent 2,520,293. Abst. in C. A. 46:134 (1952).

1137. Weissberger and Kurtzner, U. S. Patent 2,415,666. Abst. in C. A. 41: 3387 (1947).

1138. _____ and Vittum, U. S. Patent 2,384,663. Abst. in C. A. 39:5193 (1945).

1139. Wells and Riemenschneider, U. S. Patent 2,368,435. Abst. in C. A. 39:4409 (1945).

1140. _____ and Swern, U. S. Patent 2,350,435. Abst. in C. A. 38:4958 (1944).

1141. _____ and _____, U. S. Patent 2,408,897. Abst. in C. A. 41: 777 (1947).

1142. Western Electric Co., Brit. Patent 594,891. Abst. in C. A. 42:2473 (1948).

1143. Westgate, Natl. Paint, Varnish, Lacquer Assoc., Sci. Sect., Circ. No. 720, 14-20 (1947).

1144. Whitaker and Weinrich, U. S. Patent 2,443,015. Abst. in C. A. 42: 6847 (1948).

1145. _____ and _____, U. S. Patent 2,574,078. Abst. in C. A. 46: 5082 (1952).

1146. White, E. D., Food Inds., 22, 1719-21 (1950).

1147. White, E. R., U. S. Patent 2,435,333. Abst. in C. A. 42:2764 (1948).

1148. _____ and Walters, U. S. Patent 2,361,339. Abst. in C. A. 39: 4448 (1945).

1149. Widaly, Seifen-Öle-Fette-Wachse, 79, 1-4 (1953).

1150. Wiegand, Quick Frozen Foods, 8, No. 9, 81-3, 92 (1946).

1151. Williams, K. T., Bickoff and Lowrimore, Oil & Soap, 21, 161-4 (1944).

1152. Williams, L. R. and Strickland, Anal. Chem., 19, 633-4 (1947).

1153. Williamson, U. S. Patent 2,647,120. Abst. in C. A. 48:7642 (1954).

1154. Willstaedt, Swed. Patent 124,320-1. Abst. in C. A. 43:9294 (1949).

1155. _____ and Reinart, Arkiv Chem., 1, 319-24 (1949).

1156. Willstetter and Benz, Ber., 39, 3486 (1906).

1157. Wittig, Ann., 558, 201-6 (1947).

1158. _____ and Pieper, Ann., 558, 207-30 (1947).

1159. Wodsak, Fette u. Seifen, 53, 73-6 (1951).

1160. Wuest, U. S. Patent 2,489,695. Abst. in C. A. 44:2026 (1950).

1161. Yamada, Researches Electrotech. Lab., No. 443, 1-2 (1940); Chem. Zentr. 1941, I, 3494.

1162. Yates, U. S. Patent 2,440,530. Abst. in C. A. 42:5218 (1948).

1163. Yoshikawa and Nonaka, Yushi Kagaku Kyôkaishi (J. Oil Chemists' Soc., Japan), 2, 186-90 (1953).

1164. Young, U. S. Patent 2,591,651. Abst. in C. A. 46:6372 (1952).

1165. _____, U. S. Patent 2,628,212. Abst. in C. A. 47:11796 (1953).

1166. _____, U. S. Patent 2,669,507. Abst. in C. A. 48:10332 (1954).

1167. _____, Cottle and Fischer, U. S. Patent 2,625,568. Abst. in C. A. 48:729 (1954).

1168. Yourga, Food Inds., 20, 47, 146 (1948).

1169. _____, Esselen and Fellers, Food Research, 9, 188-96 (1944).

1170. Zuidema and Mitel, U. S. Patent 2,402,863. Abst. in C. A. 41:593 (1947).

1171. Zuman, Sbornik Mezinarod. Polarog. Sjezku Praze, 1st Congr., 1951 Pt. III Proc. 586-601 (in Czech.), 601-3 (in Russian), 603-5 (in Eng.).

1172. Zwergal and Umstätter, Erdöl u. Kohle, 5, 177-80, 237-40 (1952).

PART II. REDUCTION OF NITRO COMPOUNDS WITH TITANIUM III

INTRODUCTION

Quantitative determination of certain organic compounds by reduction of various functional groups with standard titanous chloride or sulfate solutions has long been practiced. This method has been especially useful in determining organic nitro compounds.

Titanous ion (titanium III) is able to lose only one electron to an oxidizing agent, forming titanium IV in the process. It has been discovered that certain oxidizing agents are able to react only if two electrons at a time are obtained from the reducing agent, while other oxidizing agents are able to react only if one electron is obtained from the reducing agent. There are some oxidizing agents which can react both ways at the same time.

Most commonly used reducing agents for the nitro group, such as zinc, iron, tin, stannous chloride, or hydrogen sulfide, are capable of reducing the nitro group with two electrons at a time. Since the oxygen requires two electrons to reach its normal reduced state, a nitroso compound, the question arises whether two electrons are necessary before a reaction will occur. Since titanium III, which can lose only one electron per ion, is a good reducing agent for nitro compounds, the manner in which the oxygen is reduced becomes of interest. By observing the kinetics of the reaction between titanium III and a nitro compound, the order of the reaction can be obtained. If it is first order in titanium III ion and nitro compound, it is implied that oxygen of the nitro group will react by accepting one electron at a time in the slow step of the reaction. If the order is first in nitro compound and second order in titanium III, then the oxygen of the

nitro group will react only if two electrons are available in the slow step of the reaction. It was the purpose of this work to find which occurred.

HISTORICAL REVIEW

Use of titanous chloride and titanous sulfate as analytical reagents in the determination of organic compounds containing functional groups which are subject to reduction has long been known and applied. A monograph[3] on the subject appeared as early as 1918. Titanous chloride reduction is often applied in the determination of organic compounds containing azo, hydrazo or nitro groups.[9]

It has been observed that certain oxidizing agents will react only if two electrons are obtained from the reducing agent at the same time, others will react only if one electron is obtained at a time, and still others will react both ways at once.[2,6,8] These conclusions were in opposition to those of Michaelis[4] and Weiss[12] who had proposed "the principle of compulsory univalent oxidation" about the same time the previous observations were made. Remick[7] was able to extend a further explanation of the observed facts and showed that the principle of compulsory univalent oxidation did not hold true in all cases.

Most commonly used reducing agents for the nitro group are such substances as zinc, iron, tin, stannous chloride, or hydrogen sulfide. These materials are capable of supplying two electrons at once to the oxygen of the nitro group. On the other hand, titanium III can only give up one electron per ion on reducing a nitro group, forming titanium IV in the process. Since each oxygen of the nitro group requires two electrons, the question arises as to whether or not the oxygen attacked will accept only one electron in the slow step of the reaction with titanium III or if two are necessary. After the first oxygen is removed, the resulting nitroso

compound is reduced more rapidly than the nitro compound, so it will not affect the kinetic order of the reactants. If two electrons are essential before the oxygen will react in the slow step, then the reaction would be second order in titanium III; if only one electron is needed, it should be first order with respect to the reductant.

This work was commenced in the fall of 1950, in order to determine whether a one electron transfer occurred or two electron transfer was essential in the slow step of the reduction of organic nitro compounds. For ten years prior to this time, interest in titanous reactions had been largely confined to analytical studies. However, since this time Johnson and Winstein[1] have reported a kinetic study of the reduction of sodium anthraquinone-2-sulfonate by titanous ion and Hinshelwood and co-workers[5] have published a paper on the reduction by titanous chloride of nitrobenzene and its derivatives which bears directly on the work reported here.

EXPERIMENTAL

Preparation of Equipment and Standard Solutions

Preparation of a nitrogen purification train

A nitrogen purification train was constructed in order to maintain a nitrogen atmosphere over the titanous sulfate solution. The nitrogen from the tank was led through two bottles of alkaline pyrogallol to absorb any oxygen which might contaminate the nitrogen. The gas was then washed with concentrated sulfuric acid to remove water vapor and then passed through Drierite and sodium calcium hydrate in a drying tower. Appropriate traps were used to prevent mixing or loss of the solutions in the train. After passing through the drying tower, the nitrogen was led into the storage bottle for the titanous sulfate solution and also into the top of an automatic burette, so that the nitrogen atmosphere could be maintained while the burette filled with titanous sulfate solution from the storage bottle. In order to maintain a constant nitrogen pressure on the system, the gas was also led from the top of the drying tower into the bottom of a bottle with a small amount of mercury in it. When the pressure became too high, the nitrogen escaped by bubbling out through the mercury and a small positive pressure was maintained on the rest of the system. Arrangements were also made so that it purified nitrogen to bubble through solutions which were being titrated, thus excluding the air.

Preparation of titanous sulfate solution by the method of Vogel[11]

Sixty ml. of commercial titanous sulfate solution (20 percent solution obtained from La Motte Chem. Products Co., Baltimore, Md.) was placed in

200 ml. of 1:3 sulfuric acid solution and boiled for two to three minutes. After cooling, the solution was diluted to two liters with carbon dioxide free water. The air in the storage bottle was displaced by nitrogen and the solution, which was approximately .0156 mole per liter, was then placed in the tank.

Preparation of 0.1 N ceric sulfate solution[13]

To 28 ml. of concentrated sulfuric acid in 500 ml. of water was added 52.8 g. of ceric bisulfate (G. Fred. Smith, Columbus, Ohio). On solution, the mixture was diluted to one liter.

Standardization of ceric sulfate

Standardization of ceric sulfate solution was accomplished by using arsenious oxide as a primary standard with ferroin indicator.[14] The iodine monochloride catalyst was prepared according to the method of Swift and Gregory.[10] The ceric sulfate solution was .0775 N. Later a more dilute solution was also prepared, which was .0153 N, by taking a volume of the above solution and diluting with four volumes of water.

Standardization of titanous sulfate

Standardization of titanous sulfate solution was performed by adding 9 ml. of ferric chloride solution (approximately .577 M) to a flask which was then flushed out with nitrogen. The titanous sulfate was added rapidly and the ferroin indicator was added. The reduced iron (ferrous) was then titrated with the standard ceric sulfate solution, the end point changing sharply from a pink to a greenish-yellow color. The normality of the

titanous sulfate was .0138 N.

Preparation of o-nitrobenzoic acid solution

A solution of o-nitrobenzoic acid (m.p. 147.5°, observed 145-147°) was prepared by dissolving 3.3416 g. in two liters of water. The solution was approximately .01 M (or .06 N) in reference to reduction by titanous sulfate.

A second solution was prepared which was .0023 M (.0138 N) in o-nitrobenzoic acid and .025 M in sodium sulfate. This solution was prepared by taking 38.33 ml. of the .01 M o-nitrobenzoic acid solution prepared above, adding 3.55 g. of sodium sulfate and diluting to one liter.

Preparation of the reaction flask

Two round bottom, standard taper flasks of 200 ml. capacity were joined by two tubes. One tube of 15 mm. size was sealed to the bottoms of the flasks and was curved upward between the flasks, having the form of an inverted "U". In this way a solution could be placed in either or both flasks without mixing, until the flask was tipped to pour it in. Just below the joint another smaller tube was run between the two flasks, so the air pressure in each would be the same during mixing. Each flask was stoppered with a stopper which had a stopcock on the end, so that air could be evacuated or flushed out with nitrogen or carbon dioxide and then the atmosphere could be excluded. Samples could be withdrawn from either flask by syringe without contamination with oxygen. A capillary tube was sealed in the flask near the top and led to the bottom of each flask. A short piece of 6/16 inch tubing was sealed to the top of the capillary and was

stoppered with small sample bottle caps. The syringe was pushed through the rubber cap, filled, taken out and the sample adjusted to 10 ml. capacity. The sample was then delivered into ferric chloride solution to quench the reaction and the analysis was begun.

Preliminary Kinetic Measurements

Run #1 (investigation of concentrations of reactants needed for easy kinetic measurement)

Fifty ml. of .0023 M (.0138 N) o-nitrobenzoic acid and .025 M sodium sulfate mixture were added to 50 ml. of .0138 N titanous sulfate solution. Both solutions were previously cooled to 20.9°. After stirring well in the volumetric flask, the mixture was again placed in the constant temperature bath at 20.9°. Ten ml. samples were pipetted out at 10 minute intervals and added to an excess of ferric chloride solution. The amount of titanous ion still present was determined by titrating the ferrous iron formed when the reaction mixture was added to the ferric chloride, thus quenching the titanous sulfate reduction of o-nitrobenzoic acid. The ferrous chloride was titrated with .0775 N ceric sulfate using ferroin as indicator. The color change was from pink to greenish-yellow.

Since this run appeared to have an initial induction period and the reaction was only about 30 percent complete in 80 minutes, it was decided to try a higher temperature. On plotting the data, it appeared that the reaction was nearer second order than any other. However, there was considerable scatter in the points and the line curved off from that for a true second order plot.

Run #2 (determination of a temperature at which to measure rates)

The same procedure was used as in Run #1 with the exception that the water bath was maintained at 24.8° and the normality of titanous sulfate solution had now fallen to .01208 N. During the latter part of the run samples were taken every 20 minutes instead of every 10 minutes. It was noted that the end point faded rapidly in the titrations with ceric sulfate using ferroin as indicator, the change being a rapid change from greenish-yellow to yellow. Titration was to the first change noted.

On plotting the data as a second order plot a curve was obtained quite similar to that of Run #1, with the exception that there appeared to have been an extremely rapid reaction between the time of mixing and the first sample, where previously an induction period was observed. Contamination by air was considered probable with oxygen reacting with titanous ion.

Run #3 (preliminary investigations of reaction order)

The same procedure was used as before, except the normality of the titanous sulfate was .0051 N. Mixing of the solution took one minute and a sample was taken after two minutes.

Runs #4, 5 and 6 (preliminary investigation of reaction order)

The same procedures were used. The normality of the titanous sulfate solution was .01206 N. Upon plotting the data from Runs 3 to 6, the same general results were obtained. The reaction between time of mixing and the taking of the first sample (usually 2 minutes from the beginning of the reaction) was much faster than the reaction which followed. The order

approached that of a bimolecular reaction. However, scattering of points on the curve was quite noticeable.

Runs #7-10 (investigation of the effects of oxygen in the air)

The normality of titanous sulfate solution was the same as in Runs 4 to 6. However, the concentration of solution of o-nitrobenzoic acid was decreased to .000767 M in the acid and .00833 M in sodium sulfate. The last two runs were commenced by putting dry ice in the reaction flasks so that carbon dioxide was generated and air excluded. Upon plotting the data of these runs, the same general results were observed as before. The dry ice eliminated some of the initial fast reaction and the points on the curves still scattered. It was decided to construct a new reaction flask from which it would be possible to exclude air during the run, even while extracting samples for titration. (See preparation of reaction flask.)

Run #11 (No reaction occurred.)

A solution (100 ml.) of .0023 M in o-nitrobenzoic acid and .025 M in sodium sulfate was placed in one side of the reaction flask and 100 ml. of .0138 N titanous sulfate was placed in the other. Evacuation was attempted but the pressure equalizing tube between the flasks was not yet in place so the solution in the second flask began to be pulled over into the first flask. Evacuation was ceased and dry ice was dropped in each flask instead. After the carbon dioxide had swept the air out of the flasks the stopcocks were closed. After mixing, the flask was placed in the 24.6° constant temperature bath. Sampling occurred at intervals during the day. No reaction to speak of occurred during the day. After six more days at room

temperature, no reaction had yet occurred, so the reaction mixture was placed in a 55° constant temperature bath for two days with the same results.

These results were disturbing, so an attempt was made to isolate the products of the reaction of the same mixture as used above in the presence of air. No definite results were obtained.

Run #12 (further investigation of concentration of reactants, temperature and catalysis)

With the surprising results of Run #11, it was decided to increase the concentration of reactants, to use the higher constant temperature bath (55°) and to add chloride ion to the mixture to see if this would catalyze the reaction, since titanous chloride is normally used in analytical procedures and the chloride ion often enters into the mechanisms of reaction when present.

In one side of the reaction vessel was placed 100 ml. of a solution .0059 M (.0356 N) in o-nitrobenzoic acid and .064 M in sodium sulfate. In the other side was placed 1.17 g. of sodium chloride and 100 ml. of .0356 N titanous sulfate. The flasks had been flushed out previously with carbon dioxide generated from dry ice and, after the solutions were added, more dry ice was dropped in to maintain the carbon dioxide atmosphere. After the carbon dioxide had been generated, the stopcocks were closed to exclude the air and the reaction vessel was placed in the 55° constant temperature bath. After the solutions had reached 55°, they were mixed together and a 10 ml. sample was removed and analyzed for titanous ion. The reaction was quite rapid. The purple color due to titanous ion was not discernible within the

first hour. Another difficulty was now encountered in the end point in the titrations to determine titanous ion. Where previous end points were changes from a clear greenish-yellow to a clear yellow color, the end point now appeared to be a dark yellow as if a brown or black or some opaque substance was also produced. For this reason, the end point was hard to read and the titrations were in error.

Runs #13 and 14 (investigation of the effect of the absence of chloride ion catalyst and lowering of the temperature of reaction)

Run #13 was conducted in the same way as Run #12, with the exception that no sodium chloride was added. Again the reaction was quite rapid with the purple color of the titanous ion disappearing in about 10 minutes. The end point of the titration to determine titanous ion gave the same difficulty as in Run #12.

Run #14 was conducted in the same way as Run #13 with the exception that the temperature was maintained at 24.6° instead of 55°. The purple color of the titanous ion disappeared after the first half-hour. After the first titration of the first sample, difficulty was encountered in detecting the end point as in the last two runs.

Runs #15 and 16 (investigation of the use of sodium diphenylamine sulfonate as an indicator in the volumetric determination of titanous ion)

Run #15 was carried out with the same concentration of reactants and the same temperature as Run #14 except the 100 ml. of titanous sulfate had decreased in concentration to .0261 N. The first 10 ml. sample was taken by syringe one minute after mixing and was added to 5 ml. of .577 M ferric

chloride. Following this, 10 ml. of concentrated orthophosphoric acid was added, and then 2 drops of sodium diphenylamine sulfonate indicator was dropped in. A very sharp end point was obtained with this and all other samples taken during the run. The color change was from colorless to purple. A blank was run to determine the error due to the added indicator.

Run #16 was carried out in the same manner and under the same conditions as Run #15 and results were similar except that practice in the titration gave more accurate data.

Upon plotting the data from Runs #14, 15 and 16, it was noted that there was a steady improvement in the accuracy of the data, in that the scattering of points became much less. The data for Run #16 gave almost a smooth curve. Similar results were obtained as previously. The curves indicated that the overall reaction was not truly second order. A first order plot for titanous ion gave a slightly curved line, while with the data from Run #16 a second order plot appeared to be possibly a straight line.

Run #17 (a check of the absence of side reactions of titanous ion)

In one side of the reaction flask was placed 100 ml. of a solution .00078 M in o-nitrobenzoic acid and .0083 M in sodium sulfate. In the other side was placed 100 ml. of .0261 N titanous sulfate, the air in the reaction flask having been expelled by carbon dioxide from dry ice. After the solutions had reached the temperature (24.6°) of the constant temperature bath, they were mixed and samples were taken at intervals for titration. If the o-nitrobenzoic acid were completely reduced, the normality of the reaction mixture should be .01075 N in titanous ion. After 114 hours

the normality was not less than .01125 N, indicating that no side reaction of any consequence was occurring. The reaction was essentially complete within 6 hours.

Since the details of the way in which the experiments were run has been presented previously, only a compilation of the essential data from the various runs which followed the solving of experimental difficulties is here presented. A sample of the data from one of the runs is included as follows:

Beginning concentration of the reaction mixture for run #21.

Titanous sulfate	.0178 N
Sulfuric acid	.696 N
o-Nitrobenzoic acid	.0356 N (.0059 M)
Sodium sulfate	.032 M

Table 7

Data from run #21

Sample #	Time after mixing	N of titanous sulfate in reaction mixture
1	1 min. 30 sec.	.0115
2	6 " 20 "	.0089
3	15 " 20 "	.0046
4	20 " 05 "	.0037
5	26 "	.0025
6	32 " 50 "	.0019
7	37 "	.0014
8	40 " 10 "	.0013
9	49 " 55 "	.0008
10	60 " 10 "	.0005
11	70 "	.0003

Table 8 which follows gives the data concerning the initial concentration of reactants in the mixture for each run. Constant ionic strength was maintained below Run #27 with the exception of Runs #32 and 33, except for changes due to change in concentration of titanous ion. Those runs marked with an asterisk proved to be too fast for accurate measurement, the reaction being 35 percent or more completed when the first sample was taken a minute to a minute and one-half after mixing.

Table 8

Initial concentration of the reaction mixtures

Run #	N of titanous ion	N of hydrogen ion	N of o-nitrobenzoic acid	M of sodium sulfate
15	.0131	1.54	.0178	.032
16	.0131	1.54	.0178	.032
17	.0131	1.54	.0023	.004
18*	.0178	.696	.178	.032
19*	.0178	.696	.089	.032
20*	.0178	.696	.0445	.032
21	.0178	.696	.0356	.032
22	.0232	.905	.0356	.032
23*	.0089	.348	.0356	.032
24	.0178	.696	.0356	.032
25	.0089	.348	.0178	.032
26	.0154	.603	.0237	----
27	.0232	.905	.0178	.032
28	.0226	.905	.0356	.032
29*	.0226	.452	.0356	.258
30*	.0226	.226	.0356	.371
31	.0178	.905	.0356	.032
32*	.0178	.452	.0356	.159
33*	.0178	.218	.0356	.277
34	.0089	.905	.0356	.032
35*	.0089	.452	.0356	.258
36*	.0089	.226	.0356	.371
Repeat 32*	.0178	.452	.0356	.258
" 33*	.0178	.226	.0356	.371

Table 8 (cont.)

Run #	N of titanous ion	N of hydrogen ion	N of o-nitrobenzoic acid	M of sodium sulfate
37	.0189	.226	.0178	.371
38	.0189	.905	.0178	.032
39	.0189	.452	.0178	.258
40	.0169	.905	.0178	.032

The concentration of various reactants in the above table were varied in a systematic way in an endeavor to learn the kinetic order of the various reactants.

DISCUSSION

Upon the compilation of the data, efforts were made to interpret the results so that the essentiality of a one or two electron transfer in the slow step from titanous to nitro compound might be determined. Since many of the reactions were quite rapid, it was decided to plot the concentrations against time on very large graph paper and determine the initial slopes. Results from this effort were very unsatisfactory until it was realized that many reactions were over 35 percent completed by the time the first sample was taken. The data from these runs were rejected and the initial slopes of the remaining runs compared. However, they were not as accurate as could be desired. It was again determined to try some first order plots of log titanous ion versus time.

If one has two reactants (one in large excess) and the rate of disappearance is followed, then the rate equation

(1) $\frac{-dA}{dt} = k[A]^n[B]^m$ becomes

(2) $\frac{-dA}{dt} = k'[A]^n$ (since $[B]^m$ is essentially constant).

Integrating, if n = 1 (first order in A), one obtains

(3) $-2.303 \log A = k't +$ constant.

If log A is plotted against time and a straight line is obtained, the reactant A is first order in the slow step of the reaction. If one ignores the calculated starting concentration of titanous ion (which is always higher than the line through the other points, thus indicating the titer of titanous ion is reduced, probably by oxygen which is not completely flushed

out of the flask), on plotting the data from four different runs good straight lines were obtained for each run, indicating that the order for titanous ion was first order. In other words, that the slow step of the reaction involves only one titanous ion, thus establishing the fact that the nitro group will accept only one electron at a time.

From the first order curves for titanous ion the following was obtained.

Table 9

Slopes and first order constants for titanous ion obtained from first order curves

Run #	Slope	First order constant (k')
22	- .0146	.0337
28	- .0158	.0364
31	- .0188	.0433
34	- .0218	.0503

Similar first order plots could not be made for the o-nitrobenzoic acid since every series in which the concentration had been varied in the presence of such an excess of titanous ion that the titanous concentration was essentially constant the speed of the reaction had been such as to make the data obtained of no value.

However, upon establishing the fact that the reaction was first order in titanous ion, it now became possible to check whether o-nitrobenzoic acid was also first order. If both reactants are near the same concentration, so that both vary during the reaction, the following equation applies:

$$(4)\quad t = \frac{2.303}{k(a-b)} \log \frac{b}{a} + \frac{2.303}{k(a-b)} \log \frac{a-x}{b-x}$$

where a and b are initial concentrations and x is the decrease in concentration after time t. If one plots $\log \frac{a-x}{b-x}$ against t, then a straight line will be obtained if the reaction is bimolecular, being first order in a and b. The slope of the curve will be $\frac{2.303}{k(a-b)}$ from which k can be calculated.

On plotting the data from 14 runs as suggested above, good straight lines were obtained with good fits to the points in every case except one. Thus the postulate that o-nitrobenzoic acid is also first order in the reaction is confirmed. The slope of each line was taken and the bimolecular constant calculated from

$$(5)\quad \text{slope} = \frac{2.303}{k(a-b)} \text{ or } k = \frac{2.303}{\text{slope } (a-b)} .$$

The data from these calculations are compiled in Table 10.

Another point of interest is the role which hydrogen ion plays in the reaction. It is easily observable that an increase in hydrogen ion concentration slows down the rate of reaction. However, of a number of runs in which hydrogen ion was varied only two were slow enough so that the data was good enough to compare. Since the rate of reaction decreases with increase of hydrogen ion concentration, the rate must be inversely proportional to some power of the hydrogen ion concentration. Since the bimolecular rate constant, as previously determined, varies with hydrogen ion concentration, it should be able to be corrected to a true specific rate constant by dividing the bimolecular rate constant by the hydrogen ion concentration raised to the appropriate power. For the results, see Table 11.

Table 10

Bimolecular constants[a] and necessary data for their calculation

Run #	Slope	(a - b)	Bimolecular constant (k)
15	- .0149	- .0047	3.29×10^4
16	- .0194	- .0047	2.53×10^4
21	- .0203	- .0178	6.38×10^3
22	- .01206	- .0124	1.542×10^4
24	- .0183	- .0178	7.08×10^3
25	- .0246	- .0089	1.052×10^4
26	- .01206	- .0083	2.31×10^4
27	+ .0052	+ .0054	8.21×10^4
28	- .0110	- .0130	1.615×10^4
31	- .0150	- .0178	8.63×10^3
34	- .02025	- .0267	4.27×10^3
38	+ .00146	+ .0011	1.432×10^6
39	+ .002125	+ .0011	9.85×10^5
40	- .00079	- .0009	3.24×10^6

[a]In this case, the concentrations have been left in terms of normality so the bimolecular constant contains these dimensions.

Table 11

Calculations pertaining to the order of hydrogen ion

	Run #38	Run #39
k	1.432×10^6	9.85×10^5
$[H^+]$	.905 N	.452 N
$\frac{k}{[H^+]}$	1.583×10^6	2.18×10^6
$[H^+]^2$	.82	.206
$\frac{k}{[H^+]^2}$	1.746×10^6	4.78×10^6

Table 12

Variation of the bimolecular constant with ionic strength

Run #	$[H^+]$	k	$\frac{k}{[H^+]^2}$	μ
28	.905	1.615×10^4	1.97×10^4	1.6242
31	.905	8.63×10^3	1.05×10^4	1.6217
34	.905	4.27×10^3	5.2×10^3	1.5554
38	.905	1.432×10^6	1.75×10^6	1.6303
40	.905	3.24×10^6	3.95×10^6	1.6153
22	.905	1.542×10^4	1.87×10^4	1.6326
27	.905	8.21×10^4	1.00×10^5	1.6326
21	.696	6.38×10^3	1.317×10^4	1.3087
24	.696	7.08×10^3	1.46×10^4	1.3087
15	1.54	3.29×10^4	1.388×10^4	2.6203
16	1.54	2.53×10^4	1.068×10^4	2.6203
25	.348	1.052×10^4	8.76×10^3	.7693
26	.603	2.31×10^4	6.36×10^4	1.1677
39	.452	9.85×10^5	4.83×10^6	1.7533

The results shown in Table 11 are disappointing, since no assignment can be made as to the order for hydrogen ion.

An effort was also made to determine what effect varying the ionic strength had on the reaction rate (see Table 12 above), but results were not enlightening. The reaction constant k was divided by the square of the hydrogen ion concentration (since Hinshelwood and co-workers[5] found the rate inversely proportional to hydrogen ion concentration) and the ionic strength was calculated for the mixture. Examination for any trends proved unfruitful.

SUMMARY

1. An investigation was made concerning whether a nitro compound can be reduced by a one electron step or whether it must have two electrons in the rate determining step to be reduced. It has been shown in this investigation that titanous ion, which can release only one electron per ion exhibits first order kinetics in the reduction of nitro compounds. Therefore, a nitro compound may be reduced by a one electron transfer in the rate determining step.

2. It has further been shown that the reaction is bimolecular with respect to titanous ion and nitro compound.

3. Although it is easily observed that the rate of the reaction decreases with increased hydrogen ion concentration, the exact dependence of the rate on hydrogen ion was not determined.

4. An unsuccessful attempt was made to discover the effect of changes in ionic strength upon the rate of the reaction.

BIBLIOGRAPHY

1. Johnson and Winstein, J. Am. Chem. Soc., 74, 3105 (1952).

2. Kirk and Browne, J. Am. Chem. Soc., 50, 337 (1928).

3. Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis", Longmans, Green and Co., London, New York (1918).

4. Michaelis, Ann. Rev. Biochem., 7, 1 (1938).

5. Newton, Stubbs and Hinshelwood, J. Chem. Soc., 3384 (1953).

6. Remick, "Electronic Interpretations of Organic Chemistry", 2nd Ed., John Wiley and Sons, New York, New York (1949).

7. _____, J. Am. Chem. Soc., 69, 94 (1947).

8. Shaffer, J. Am. Chem. Soc., 55, 2169 (1933).

9. Siggia, "Quantitative Organic Analysis Via Functional Groups", 2nd Ed., John Wiley and Sons, New York, New York (1954).

10. Swift and Gregory, J. Am. Chem. Soc., 52, 901 (1930).

11. Vogel, "Quantitative Inorganic Analysis", Longmans, Green and Co., London, New York (1939).

12. Weiss, J. Chem. Soc., 309 (1944).

13. Willard and Diehl, "Advanced Quantitative Analysis", D. Van Nostrand Co., Inc., New York, New York (1943).

14. _____ and Furman, "Elementary Quantitative Analysis", D. Van Nostrand Co., Inc., New York, New York (1940).

ACKNOWLEDGMENTS

The author would like to express his appreciation for the patient guidance and encouragement received during the course of this work from Dr. George S. Hammond.

The author is also indebted to the B. F. Goodrich Company for financial support during much of this investigation.