utilized to plasticize certain of its compounds. Their noncorrosive property makes them inactive in protective coatings. Basic pigments can be used without fear of livering since the acid number is usually less than 0.2. Coatings based on Tornesit and Pliolite require plasticizing agents to modify these finishes.

These oily polymers are useful in lowering the melting point of any coumarone-indene resin to a certain desired temperature; they also make such resins soluble in petroleum oils. Most natural synthetic gums and resins are compatible with them. Aluminum pastes and paints have unusual leafing qualities when these oils are introduced into their formulas.

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Drying Oils and Resins

Influence of Molecular Structure upon Oxygen and Heat Convertibility

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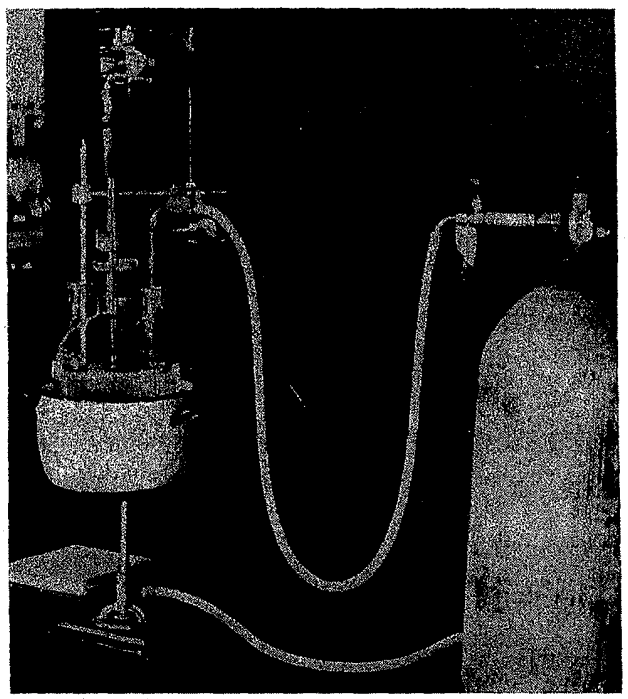
A considerable number of simple and of more complex esters of the fatty acids of linseed and of tung oils were prepared and evaluated with respect to their oxygen and heat convertibility. The heat-nonconvertible systems were also oxygen-nonconvertible, and the oxygen-convertible or "air-drying" compounds were generally restricted to the heat-convertible systems.

The ability to undergo oxygen conversion is governed by the molecular structure of the reactants, requiring, as in the case of heat convertibility, the use of polyfunctional reactants, at least one of which must be more than bifunctional. As a secondary requirement, at least one of the reactants must contain functional groups which are capable of being activated and caused to react by means of oxygen, thus differing from the heat-convertible systems only in the form of reactivity of the functional groups, which obviously is then related to the specific nature of these groups.



APPARATUS FOR PREPARING MONO- AND DIGLYCERIDES

IN A PREVIOUS communication (*1*) it was maintained from principally theoretical considerations that the so-called drying of the drying oils and resins is but a typical manifestation of that more general phenomenon which consists of the transformation of an organic substance from an essentially linear structure to the so-called three-dimensional polymeric form. If such is the case, then theory further predicts that the drying characteristics of the oxidizable oils and resins must be determined by structural factors identical with those which determine the conversion of other systems—i. e., the number of reactive or functional groups per molecule of reactant. Additional factors should appear which are related to the ultimate mechanism of the conversion and in this case must obviously involve oxidation. These latter may be contrasted with the conversion of the same or of other systems by such other means as heat, light, sulfur, etc.; from them we may reason that the exact mechanism of the conversion will be determined mainly by the specific nature or type of reactivity of the functional groups.

Therefore, we may advance the following postulates:

1. The so-called drying of the drying oils and resins is but a physical transformation involving a conversion of these substances from an essentially linear structure to a three-dimensional polymeric form.
2. This physical transformation, as in any other conversion, requires that the interacting molecules be polyreactive, and that at least one of the reactants be polyreactive to the extent of 3 or more.
3. The mechanism of this conversion, as of any other conversion, is governed by the specific nature of the reactive or functional groups; it requires, in the case of the drying oils and resins, a plurality of groups which are capable of reacting with oxygen; or in any other case, it requires that particular form of matter or of energy by means of which we desire the ultimate conversion to be effected.

In applying postulates 2 and 3, as previously indicated, it is necessary to go somewhat beyond the original Kienle (*7*) and Carothers (*2*) concepts and to distinguish between the potential and the actual functionality of compounds in order to determine their degree of polymeric reactivity.

Application of these concepts to the interpretation of many of the experimental data relating to the drying oils that have accumulated during the last twenty years has led to the conclusion that the normal degree of functionality of the more unsaturated fatty acids of the natural drying oils is but two; therefore drying esters of such acids were observed only in the case of esters derived from alcohols possessing a functionality of 3 or more.

Since these conceptions of the drying oils and resins and of their drying processes differ considerably from those older ideas which were predicated so largely upon colloidal concepts or upon postulated variations of oxidation and of polymerization mechanisms of undetermined nature, it now becomes imperative to examine the experimental evidence.

The present communication is concerned with a portion of this evidence and relates to observations concerning the influence of molecular structure upon the oxygen and the heat conversion of a number of unsaturated esters.

Esters of Fatty Acids from Linseed and Tung Oils

Drinberg and Blagonravova (*4*) recently confirmed and extended the observations of earlier investigators to the effect that those esters of the fatty acids of linseed oil which are derived from saturated monohydric alcohols are oxidizable and yet remain liquid and nonfilm-forming. They likewise showed that the ethylene and propylene glycol esters form only soft, plastic coatings which remain almost completely soluble in petroleum ether. They succeeded in obtaining insoluble, well-converted, or dried films only in the case of those esters derived from polyhydric alcohols containing three or more hydroxyl groups.

Their observations with respect to the oxygen convertibility of the linseed esters are closely paralleled by the earlier observations of Fonrobert and Pallauf (*5*) with respect to the heat convertibility of tung oil esters, for heat convertibility was not attained in the case of the free fatty acids or of the ethyl or glycol esters but only in the case of the glycerides. Moreover, the triglyceride was found to be readily heat-convertible, but the mono- and diglycerides were heat-convertible only after additional heating under conditions which were considered to have produced decomposition or rearrangement with probable formation of triglyceride.

It becomes interesting and important to extend this work and particularly to determine whether there is any relation between the heat and the oxygen convertibility of such compounds, and if so, its possible significance.

Preparation of Esters

Commercially distilled fatty acids of linseed oil and a light-colored commercial grade of tung oil fatty acids were used for the preparation of the ethyl esters, the ethylene glycol monoesters, and the glycerol mono- and diesters by the methods of Long and his associates (*9*). Triglycerides in the form of linseed and tung oils were likewise included in the experiments to be described. Analytical values are shown in Table I.

These values show the fatty acids and the triglycerides to be of characteristic commercial quality. The esters prepared from these acids underwent, in the case of the monoglycol and mono- and diglyceride esters, partial polymerization during their formation. Moreover, as was first observed by Long and his associates (*9*), an excess of from 15 to 20 per cent of water over the theoretical was collected during these esterifications which may be attributed to polyglyceride

TABLE I. ANALYTICAL DATA

Material	Density		n_D^{20}	Acid No.	Saponification No.	Wijs Iodine No.	Acetyl No.	Viscosity (25° C.) Poises
Linseed acids	0.9014	d_{25}^{25}	....	202	...	183	...	...
Tung acids	0.9140	d_{40}^{40}	....	200.6	...	157	...	...
Linseed oil	0.9254	$d_{15.5}^{25}$	1.4797	2.0	191.8	185.9	...	...
Linseed ethyl esters[a]	0.8766	$d_{15.5}^{27}$	1.4595	7.9	...	...	...	...
Tung oil	0.9435	$d_{15.5}^{15.5}$	1.5172	3.6	195.7	169.6	...	...
Tung ethyl esters[b]	0.8870	$d_{15.5}^{27}$	1.4841	8.7	...	...	...	...
Linseed monoesters of ethylene glycol	0.9214	$d_{15.5}^{30}$	1.4748	2.7	171	...	168	0.5
Tung monoesters of ethylene glycol	0.9495	$d_{15.5}^{30}$	1.4956	1.7	175	...	130	2.25
Linseed monoesters of glycerol	0.9818	$d_{15.5}^{30}$	1.4785	1.8	166	...	288	1.4
Linseed diesters of glycerol	0.9314	$d_{15.5}^{30}$	1.4777	5.0	184	...	81.2	0.6
Tung monoesters of glycerol	0.9934	$d_{15.5}^{27}$	1.4996	2.5	161	...	308	36.2
Tung diesters of glycerol	0.9718	$d_{15.5}^{27}$	1.5000	4.5	182	...	83.3	63.3

[a] Boiling point, 190–196° C. at 4 mm.
[b] Boiling point, 190–211° C. at 4 mm.

formation. Partial polymerization by addition and condensation reactions appears to be an unavoidable consequence of the required conditions for these esterifications—i. e., 5 to 11 hours at 200° to 205° C. While recognizing the existence of these side reactions and the consequent impurity of the esters, it is believed that their value was not materially impaired for present purposes; indeed, similar reactions are commonly encountered during the heat-bodying of varnish oils without loss and very frequently with improvement of oxygen and of heat convertibility.

Oxygen Convertibility. Solutions of the various esters at 15 per cent concentration in xylene were prepared in duplicate; in one set was admixed 0.5 per cent lead and 0.05 per cent of cobalt in the form of naphthenate driers calculated on the fatty acid equivalent of each. Calculated volumes (averaging 3.5 cc.) were pipetted onto glass plates[1] (4 × 6 inches) which were held level by flotation on mercury.

Upon evaporation of the solvent, coatings of good uniformity (0.0008 to 0.0009 inch thick) were obtained. The plates were then exposed to the air at room temperature over a period of 15 months. The drying characteristics were observed closely during the first week and thereafter at frequent intervals. After 15 months the coatings were spot-tested with acetone to determine their relative solubility and were then subjected to localized heat to determine their relative fusibility. The results are given in Table II.

Table II. Oxygen Conversion

Material	Observed Characteristics during 15 Months at Normal Temperature
Linseed acids	Formed only soft coatings of irregular surface, slightly tacky at room temp.; dissolved by acetone, melted below 100° C.
Tung acids	Similar to linseed acids; sol. in acetone and easily fusible below 100° C.
Linseed ethyl esters	Remained in liquid condition with slight viscosity increase; easily sol. in acetone
Tung ethyl esters	Same
Linseed monoesters of glycerol	Formed only soft tacky coatings which dissolved in acetone and melted below 100° C.
Tung monoesters of glycerol	Same
Linseed diesters of glycerol	Same
Tung diesters of glycerol	Formed partially converted films; slightly tacky, increasing in tackiness with elevation of temp. but not fusing; softened but not dissolved by acetone
Linseed oil	Formed nontacky well-converted film, not fusible at 250° C.; insol. in acetone
Tung oil	Without drier, yielded frosted or opaque coating; with drier, a transparent and glossy film somewhat "gas checked"; in each case, films were not fusible or unduly softened at 250° C. and were insol. in acetone

These tests showed that the free fatty acids of linseed and of tung oils, their ethyl esters, and their monoglyceride esters are incapable of drying to yield films of the infusible and insoluble type under these conditions. The linseed diglyceride ester was similarly observed to be nondrying or nonconverted; the corresponding tung ester, however, closely approached a converted or dry state.

Well-converted films of the insoluble and infusible type were obtained from the triglyceride esters of tung and of linseed acids.

The use of metallic drier was observed to accelerate the oxygen conversion of the convertible systems, but to confer no such conversion upon those systems which had remained nonconverted in the absence of drier.

With the exception of the tung diglycerides the observed characteristics are strictly in accordance with the theory. The partial yet fairly substantial conversion of the tung diglycerides may be due to the proportion of triglycerides or polyglycerides in them or to the development of a slightly greater degree of functionality than is normal through activation and reaction of additional points of unsaturation. The exact cause remains to be established.

Heat Convertibility. Test tubes were charged with 10-gram samples of the foregoing substances and were simultaneously heated in a well-agitated oil bath. The temperature was raised to 280° C. during a period of 45 minutes and was maintained at that point.

Conversion of the free fatty acids and of the ethyl esters was not accomplished. Conversion of the remaining esters to the infusible, insoluble form was observed as follows:

Material	Time to Gel after Reaching 280° C. *Min.*	Obsvd. Loss in Weight %
Tung oil	10	0.05
Tung diglyceride	70	0.89
Tung monoglyceride	100	7.8
Linseed oil	220	3.3
Linseed diglyceride	280	6.1
Linseed monoglyceride	360	11.5

The observed and well-recognized more rapid heat conversion of the tung esters *vs.* the corresponding linseed esters is a characteristic which has generally been attributed to the greater reactivity of the conjugate unsaturation of the eleostearin of tung oil and requires no particular comment.

The observed reduction in the velocity of the heat conversion of the tung and linseed esters which accompanies the change of structure from the triglyceride to the mono- and diglyceride form is, however, very important. In this case we observe a departure from the normal concurrence of heat and of oxygen convertibility. Why should their oxygen convertibility suffer such loss as compared to their heat convertibility? Detailed evidence has yet to be gathered. It may, however, be observed that the eventual heat conversion of the mono- and diglycerides is accomplished only after substantially greater loss of volatile matter than in the case of the triglycerides and also that this loss is greater in the case of the monoglycerides than in the case of the diglycerides. Such behavior is to be expected if the mono- and diglycerides decompose and eliminate their excess glycerol with formation of the triglyceride or, as seems more probable, undergo polyglyceride formation through etherification with elimination of water. In either case, eventual heat conversion may be expected; yet because these same reactions are not affected by oxygen, they may not be expected to lead to an oxygen conversion.

Interdependence of Heat and of Oxygen Convertibility

From such considerations it was suspected that the relatively nonoxygen-convertible linseed mono- and diglycerides and tung monoglyceride should be capable of being changed into oxygen-convertible forms simply by additional heating under conditions which would favor condensation polymerization. Therefore, the foregoing were heated in open containers at 275–280° C. during a period of 6 hours, with observed weight losses as follows:

Tung monoglycerides	7.3%
Linseed monoglycerides	10.0
Linseed diglycerides	5.0

[1] In the few cases where drying was not expected, shallow tin trays of approximately this size were substituted for the glass panels in order to prevent mechanical loss of the liquid.

Seven-gram samples were diluted with equal weights of xylene and drier equivalent to 0.15 per cent lead and 0.05 per cent cobalt based on the oil content. The original mono- and diglycerides were included as controls. The solutions were flowed on glass slides in duplicate; one set was dried at room temperature and the other at 120° C. The following observations were made:

AT ROOM TEMPERATURE. During 24 hours all of the heat-treated mono- and diglyceride coatings were observed to yield acetone-insoluble well-converted films possessing but little surface tack. Partial or no conversion was observed in each of the controls.

AT 120° C. During 30 minutes only the heat-treated glycerides had formed films. In another 30 minutes these films were found to be acetone-insoluble and to possess but slight surface tack. The controls were only partially converted to insoluble form, being extremely soft and sticky.

Although these observations require additional and more detailed investigation, their probable significance is already apparent and, upon confirmation, should prove helpful in extending our knowledge of the drying and polymerizing phenomena, particularly those which pertain to the interdependence of heat and of oxygen convertibility.

Oxygen-Convertible Resins

Kienle (*6*) described oxygen-convertible or air-drying resins of the alkyd type in which the more unsaturated and oxidizable fatty acids are caused to enter into combination with phthalic anhydride and glycerol or their equivalents. The patent literature specifies many supposed equivalents. This literature would lead us to believe that the mere condensation of a drying-oil fatty acid with a polybasic acid and a polyhydric alcohol, or with an intermediate condensation product of the two, is sufficient to produce an air-drying resin.

The incorporation of the more highly unsaturated fatty acids in condensation polymers of the alkyd type might be expected to result in products which would be capable of reacting with oxygen, provided the unsaturation was not destroyed or rendered ineffective during the condensation. But if drying is merely one form of conversion—i. e., oxygen conversion—then the mere fact that a particular ester or condensation polymer happens to be oxidizable cannot be said to ensure that it will "dry" upon oxidation. Failure to appreciate this point or properly to distinguish between oxygen convertibility and oxidizability is unfortunate and is believed to have thus far served only to obscure the fundamental nature of the drying processes.

It is therefore hoped that the following experimental observations may serve to clarify this situation, to help establish a new conception of the drying of oils and of resins, and to promote such additional research as will contribute to further progress.

PREPARATION AND TESTING OF RESINS. Alkyd resins were prepared from gram-mole proportions of the following reactants by direct reaction in round-bottomed Pyrex glass flasks at 180° to 200° C. in an atmosphere of carbon dioxide. The reaction was continued in each case until polymerization was well advanced as determined by the well-known string test or until it became evident that no heat conversion was likely to occur:

Compn. No.	Reaction Time	Glycerol	Ethylene Glycol	Phthalic Anhydride	Linseed Acids	Tung Acids	Softening Point[a]	Acid No.	Viscosity of 50% Soln. in Xylene (at 25° C.)
	Hr.	*Mole*	*Moles*	*Moles*	*Mole*	*Mole*	*° C.*		*Poises*
1	11	1	...	1.25	0.5	...	52	86	60
2	5.75	1	...	1.25	...	0.5	57	47	9
3	31	.	1.5	1.25	0.5	...	8	18	<0.5
4	31	.	1.5	1.25	...	0.5	33	28	<0.5

[a] A. S. T. M. ring and ball method.

Oxygen conversion or drying tests were made according to the previously described method over a period of 15 months. Within 12 to 24 hours compositions 1 and 2 yielded dry films which were then infusible and insoluble in acetone. Compositions 3 and 4 provided coatings which, during 15 months of observation, remained soft and tacky, were soluble in acetone, and were fusible below 120° C.

Does this indicate that only the glycerol or higher polyhydric alcohol esters will dry, and that drying esters will not result in the case of the corresponding glycol esters? In the attempt to answer this question the following experiments were conducted:

Compn. No.	Ethylene Glycol	Polybasic Acid	Linseed Acids	Tung Acids
	Gram-mole	*Gram-mole*	*Gram-mole*	*Gram-mole*
5	0.5	Citric acid, 0.25	0.25	...
6	0.5	Citric acid, 0.25	...	0.25
7	0.114	Tricarballylic acid, 0.057	0.057	...
8	0.114	Same	...	0.057
9	0.5	Tribasic acid adduct of maleic anhydride and eleostearic acid, 0.25	0.25	...
10	0.5	Same	...	0.25

These alkyd esters were prepared by methods determined by the characteristics of the reactants. Although polybasic acids, with but few exceptions, can be successfully employed for the production of alkyd resins by routine methods, it becomes necessary in certain cases (as when the acids are easily decomposable, relatively infusible, or too high in melting point, or are relatively insoluble and incompatible with the desired other reactants) to modify the methods of procedure. Thus in the case of compositions 5 to 10, inclusive, it was found helpful first to combine the unsaturated acids with a mole equivalent of the glycol and subsequently to cause this to react with the remaining constituents. For this purpose the monolinseed and tung esters of ethylene glycol (Table I) were employed. In addition, it was necessary in the case of resins 5 to 8, inclusive, to carry out these reactions in the presence of an inert, mutual solvent. Camphor was used for this purpose. Thus citric and tricarballylic acids were combined with the monoglycol esters in the presence of three times their weight of camphor under conditions which permitted the camphor to distill slowly; the reaction was extended until a homogeneous product was obtained. Distillation was continued until all but the last traces of camphor were removed, the excess glycol was then added, and the reaction was continued at 200° to 225° C. in the presence of an inert gas until sufficient viscosity had been attained.

Solutions of resins 5 to 10 were included among the previously described "drying" tests, and in each case, both with and without the addition of metallic drier, they dried quickly upon exposure to the air to yield infusible, acetone-insoluble films.

Of equal interest and importance were the following experiments:

Compn. No.	Ethylene Glycol	Dibasic Acid		Linseed Acids
	Gram-mole	*Gram-mole*		*Gram-mole*
11	0.15	Succinic	0.125	0.05
12	0.15	Adipic	0.125	0.05
13	0.15	Sebacic	0.125	0.05
14	0.15	Maleic	0.125	0.05

Reaction of these mixtures was carried out in the normal manner in the presence of carbon dioxide and under conditions which permitted the free escape of water of reaction. The temperature in each case

was brought to 200° C. in one hour and to 225° in another 20 minutes. Reaction 14 was discontinued after 13 minutes on account of extensive polymerization. The remaining mixtures were reacted for 3 hours, cooled, and dissolved in xylene:

Compn. No.	Acid No.	Viscosity of 50% Soln. in Xylene at 25° C. *Poise*
11	4.0	Solidified as crystalline mass
12	9.8	<0.5
13	2.6	<0.5
14	10.4	0.85

Air-drying characteristics with production of infusible and acetone-insoluble films were observed only in the case of composition 14. Converted films of this resin were obtained in 3 days without drier and within 12 hours with drier.

The same compositions were then applied to tin panels and were stoved at a temperature of 140° C. in the presence of air. Light-colored well-converted films of composition 14 were obtained in 15 minutes under these conditions. Conversion of the remaining members occurred only in from 10 to 14 hours, accompanied by severe discoloration.

Interpretation and Conclusions

The free fatty acids of linseed and of tung oils and their ethyl esters are neither air-drying nor heat-convertible, whereas the triglycerides of these acids are both air-drying and heat-convertible. This confirms the work of prior investigators who have also shown the corresponding glycol esters to be nonheat-convertible and nonair-drying.

The air-drying properties of tung and of linseed oils are destroyed or impaired by rearrangement of structure from the triglyceride to that of the mono- or diglyceride form. This loss of air-drying characteristics is also accompanied by a partial reduction but not a loss of the heat convertibility. This loss is partially or wholly compensated for, and air-drying properties are restored by subjecting the mono- and diglycerides to conditions which are known to promote condensation polymerization.

Complex esters of the alkyd type have been prepared from a number of polybasic acids and from glycerol and ethylene glycol with further modification by use of the fatty acids of linseed and of tung oils. It was observed that such modification resulted in air-drying resins only in the case of those systems which are known to be of the heat-convertible type. Failure to air-dry was observed only in the case of the heat-nonconvertible systems. Several of the nonair-drying and nonheat-convertible systems were observed to have dried or undergone conversion when subjected to the combined action of heat and of oxygen during an unusually extended period of time.

These observations are considered to be highly significant. The apparent relation between the heat convertibility and the air-drying qualities is considered as definite evidence that the so-called air-drying characteristics are in part determined by the same factors which determine the heat convertibility of the same and which therefore are unrelated to the oxidation mechanism.

These factors are clearly shown to involve the number of reactive or functional groups per molecule of the reactant regardless of their specific nature. Thus not only do carboxyl and hydroxyl groups but also, under certain conditions, the carbon-to-carbon double bonds count as polymeric functions. When the carbon-to-carbon double bonds are present in the benzenoid form (as they occur within the phthalate radical), there is no evidence of functionality. In the case of the maleic radical it has been shown that the unsaturation becomes functional; this is likewise true in the case of the drying-oil acids. Pending the publication of detailed experimental evidence, it is proposed to assign tentatively a polymeric functionality of 2 to the carbon-to-carbon double bond of the maleic radical and of only 1 to the entire unsaturated system of the more unsaturated acids of linseed and of tung oils. It is possible, then, to assign functionality equivalents to the various reactants of the present investigation as follows:

Bifunctional Reactants	Reactants Which Are More than Bifunctional
Ethylene glycol	Glycerol (3)
Phthalic anhydride	Citric acid (3 or more)
Succinic acid	Tricarballylic acid (3)
Adipic acid	Tribasic adduct of maleic and eleostearic acids (3 or more)
Sebacic acid	
Linoleic acid[a]	
Linolenic acid[a]	
Eleostearic acid[a]	Maleic anhydride (4)

[a] Normally but 2, yet may become greater under unusual conditions.

It is then perceived that air-drying or oxygen-convertible esters were not obtained from the drying-oil acid modifications of bifunctional reactants. Air-drying compositions were obtained only from similar modifications of the more polyfunctional reactants or from reaction mixtures which contained at least one of these. But as Kienle (7) has shown, the same degree of functionality is likewise required for the production of heat-convertible polymers. This furnishes solid ground for the belief that the so-called air-drying of certain oils and resins is but one form of conversion[2] or of the transformation of linear molecules to their so-called three dimensional polymeric form. The observed data are therefore seen to support postulates one and two.

With respect to postulate 3, it is obvious that the requirements for heat and for oxygen convertibility are only numerically identical. Carboxyl and hydroxyl groups are functional with respect to heat condensation yet not with respect to activation by oxygen. An oxygen-activatable group is required for an oxygen-convertible resin. Certain forms of unsaturation are required, such as in the case of the drying-oil acids. It may further be reasoned that the well recognized activity of the latter toward both heat and oxygen may be presumed to account for the observed relations of the oxygen and of the heat conversions of these unsaturated esters.

The close relation of the oxygen and of the heat conversions of the drying oils and resins is considered indicative of the probability that no greater number of functional groups is involved during an oxygen conversion than during a heat conversion.

With respect to the relative effect of the potential *vs.* the actual degree of functionality which is developed during a polymerization, the present work is likewise suggestive. In the case of the mono-, di-, and triglycerides we have, on the one hand, glycerol which is potentially trifunctional but which attains this degree only in the case of the triglyceride, being difunctional in the diglycerides and monofunctional in the monoglycerides. With respect to further condensation, the diglyceride then becomes monofunctional and the monoglyceride bifunctional. This functionality can be exercised only by etherification of these hydroxyl groups, unless additional acid is introduced to permit of further esterification. Etherification can be induced by high temperatures yet not by oxygen; therefore the mono- and diglycerides may be made to undergo a heat conversion but not an oxygen con-

[2] Kienle and Ferguson (7) were perhaps the first to refer to "air-drying" in terms of "oxygen conversion." They did not, however, relate oxygen conversion to heat conversion, preferring instead to consider these in separate categories. Such a classification may have served to obscure the fact that drying-oil acid modified alkyd esters are not air-drying unless the functionality of the reactants is greater than that of a bi-bifunctional system and to delay the recognition of the fundamental nature of the so-called oxygen conversion. Kienle and Winslow (8) partially remedied this situation but did not correlate the phenomena of heat and of oxygen conversion.

version unless sufficient heat conversion has previously been accomplished. In the case of these same glycerides and of other esters of the drying-oil acids, we have also, on the other hand, acids which have the potential functionality of their unsaturation, ranging from 4 to 6; but ordinarily this unsaturation is apparently developed only to the extent of 1. If by suitable modification of the reaction conditions we can bring more of this potential functionality into play, it should then be possible to advance the degree of polymerization. The observed heat conversion of the mono- and diglycerides as well as the ultimate conversion of certain of the nonair-drying resins of this experiment under the combined action of heat and of oxygen are believed to be due to just such factors. Further and more conclusive evidence relating to the characteristic effect of this potential but delayed functionality will be forthcoming.

Perhaps one of the more important observations that may be made as a result of the present work relates to the observed mutual and apparently equivalent effect of various functional groups in determining the degree of the polymeric state. Thus, active carbon-to-carbon double bonds may serve fully as well as carboxyl and hydroxyl groups in those "hybrid" systems in which both may become operative. Nature thus seems to regard addition and condensation mechanisms as but two means of attaining the polymeric state. It is just such evidence which favors a general revision of the definition of polymerization such as has been advocated by Carothers (*3*).

Acknowledgment

The writer gratefully acknowledges the invaluable assistance of his associates, L. P. Moore, R. T. Dean, W. C. Norris, V. Bishop, and W. B. Johnston, in connection with the preparation and analysis of a number of the compositions here described. Particular credit is also due W. M. Grosvenor and G. M. J. Mackay for valuable help and criticism and to the American Cyanamid Company for its support of this work and the permission to publish it.

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Correction

An error has been brought to my attention which occurred in my article on "Fluid Flow Design Methods" [INDUSTRIAL AND ENGINEERING CHEMISTRY, 29, 385–8 (1937)]. In the table of nomenclature on page 388 the symbol G is given as mass velocity, lb./(hr.) (sq. ft.); the time element should be seconds instead of hours.

R. P. GENEREAUX

Prevention of Calcium Deposits in Process Waters

Relative Value of Sodium Metaphosphate and Pyrophosphate

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Sodium metaphosphate and sodium pyrophosphate are compared on the basis of their relative effectiveness in preventing the precipitation of calcium orthophosphate, calcium carbonate, and calcium soaps. Sodium metaphosphate is more effective than sodium pyrophosphate both on the basis of the relative quantities necessary to prevent precipitation and of their relative tolerance for calcium ion in the presence of the precipitants studied.

RECENT investigations in the science of water-conditioning which have culminated in the development of a new product, sodium metaphosphate (glassy), and a new process (*4*) for the softening of water, have suggested the approach to the study of the prevention of calcium deposits in process waters described in this paper. It deals with the precipitation that takes place in industrial cleaning operations when alkaline salts are employed as cleaning agents in untreated waters. In practically every field of industrial cleaning, especially in the food industries which include the dairy, bottling, and beverage fields, the preferred cleaning agents are the alkaline salts, trisodium phosphate, sodium metasilicate, and sodium carbonate. These salts are used for reasons of efficiency, economy, and adaptability to commercial equipment. However, in spite of their recognized efficacy as detergents, they have one failing that is common to all. Because of the insolubility of their alkaline