TRANSACTIONS AND COMMUNICATIONS

Some Recent Advances in the Chemistry and Technology of Drying Oils*

By G. H. HUTCHINSON

INTRODUCTION

Much has been added to our knowledge of the chemistry of drying oils over the past twelve to fifteen years. It is the object of this paper to survey some of the important advances, and against this fundamental background to discuss a number of technical developments in processed drying oils. Rather than present a general review a limited number of topics will be discussed in an attempt to show how much industry has come to depend on fundamental research for a better understanding of its technical oil media, and to stimulate ideas for new developments in drying oils. Reference will also be made to some work carried out in the author's laboratory on the heat treatment of drying oils.

THE POLYESTER CONCEPT OF DRYING OIL POLYMERS

In the earlier studies on drying-oil polymerisation a good deal of attention was paid to studies of addition reactions and the role of the unsaturation of drying oils. The knowledge that drying-oil polymers could be formed by condensation as well as by addition reactions came as a result of studies on alkyd resins and other polymers. With the recognition that drying-oil polymers are polyesters, new knowledge is being gained of the behaviour of drying oils on thermal and oxidative treatment and during the complex processes of film formation. It will be useful to dwell a little longer on this aspect of polymer chemistry.

The functionality requirements of acids and alcohols, which in condensation reactions lead to the building up of polymers, are that reaction between a dihydric alcohol and a dimeric acid leads to the formation of a linear polymer. while reaction between a trihydric alcohol and a dimeric or trimeric acid leads to the formation of a three-dimensional polymer. It can be seen that a stand oil formed by heat treatment of unsaturated drying-oil glycerides may be regarded as a polyester formed by reaction of glycerol with a mixture of mono-, di- and tribasic acid units. Stand oils are not in fact manufactured in this way, but the final product is the same, whether it is made by esterifying the mixed polymeric acids with the alcohol, or by thermal treatment of the drying-oil glycerides to give the same degree of polymerisation. When the so-called *modified drying oils* are synthesised the reactivity of the drying oil molecules is generally increased, *e.g.*, by replacement of the alcohol or fatty acids with polyols or polybasic acids of higher functionality. The polyester concept applies not only to stand oils, blown oils and modified drying oils, but also to the formation of dried films. In the manufacture of a stand oil the ester polymer is built up to a stage short of the gel point. When this product is incorporated in a paint and the latter is applied in film form, the *polyesterification* is carried to the gel stage by the linking together of further monomeric (monobasic) acid units. This linkage is brought about following oxidation of the reactive centres

*Read before the Hull Section on 7 October, 1957.

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The fatty-acid composition chart (Table of a number of drying and semi-drying oils.

TABLE I

COMPONENT FATTY ACIDS OF DRYIN

Oil	Iodine Value	Saturated Acids	Oleic Acid	Linol Acic
Perilla ..	205	7	20	5
Conophor ..	200	11	12	12
Linseed ..	180	10	20	20
Candlenut ..	164	13	10	49
Rubber seed..	138	21	20	38
Soya Bean ..	133	19	22	50
Niger seed ..	136	15	15	66
Sunflower seed	136	10	22	68
Safflower seed	133	7	26	67
Tobacco seed	142	5	27	66

*Len × (Lin ÷ Len) × 10^{-2}.
†(Lin ÷ 2Len)
where Lin = % Linoleic acid. Len = % Linolenic

in the fatty-acid chains. On drying, the film contains only a relatively small proportion of polymer and a high proportion of unchanged but still reactive material. Hardening and ageing leads to a highly cross-linked polymer structure.

Constitutive Aspects of Drying-Oil Chemistry

A great deal of attention has been given to studies of this nature in recent years. Development of new analytical techniques, such as low-temperature crystallisation of fatty acids and glycerides from solvents and spectrophotometric analysis, has made it possible to obtain more accurate information about the constituent fatty acids of the technical drying and semi-drying oils used in the surface-coating industry. Attention may be drawn to Hilditch's latest edition of *The Chemical Constitution of Natural Fats*[1], which includes most of the relevant results up to 1955.

In 1943 Hilditch suggested that, in searching for additional sources of oils for the surface-coatings industry, more attention should be given to studies of component fatty acids and glycerides in the oils under consideration. The acute shortage of drying oils in the years following the end of World War II made studies of this kind of vital importance to industry. Much work has been carried out in this country, on the Continent, in India, and in the U.S.A. on constitutive aspects of paint oils; perhaps the greatest contribution to this field has been made by Hilditch and the Liverpool School.

The fatty-acid composition chart (Table I) shows the fatty-acid composition of a number of drying and semi-drying oils. Although these are typical analyses,

TABLE I

Component Fatty Acids of Drying and Semi-Drying Oils

Oil	Iodine Value	Saturated Acids	Oleic Acid	Linoleic Acid	Linolenic Acid	Total *Drying* Acids	Drying Power	
							Hilditch Index*	Greaves Index†
Perilla ..	205	7	20	5	68	73	50	141
Conophor ..	200	11	12	12	65	77	50	142
Linseed ..	180	10	20	20	50	70	35	120
Candlenut ..	164	13	10	49	28	77	22	105
Rubber seed..	138	21	20	38	21	59	12	80
Soya Bean ..	133	19	22	50	9	59	5	68
Niger seed ..	136	15	15	66	4	70	3	74
Sunflower seed	136	10	22	68	0	68	0	68
Safflower seed	133	7	26	67	0	67	0	67
Tobacco seed	142	5	27	66	2	68	1	70

*Len × (Lin ÷ Len) × 10^{-2}.
†(Lin − 2Len)
where Lin = % Linoleic acid. Len = % Linolenic acid.

it is important to bear in mind that considerable variation in fatty-acid composition can occur in any botanical species, due to factors such as climatic conditions during seed development. In the last two columns of the chart are figures calculated from the so-called *quick-drying* index which has been used as an estimate of drying power of an oil from a consideration of its component linoleic and linolenic acids. The index derived by Hilditch[2], Len × (Lin ÷ Len) × 10^{-2}, does not assign drying power to oils containing solely linoleic acid in their constituent acids. That by Greaves[3], (Lin + 2 Len), is of more general value, since by its use values can be assigned to the linoleic-rich oils, such as tobacco seed, safflower, sunflower, poppyseed, etc. However, the need for *indices* of this type is passing, since with a new knowledge of the glyceride composition of drying oils, the drying properties of an oil may be directly assessed so far as glyceride composition is concerned from the proportions of linolenic and linoleic acid in its component acids[6]. Non-conjugated drying oils can be divided into two classes, linolenic-rich and linoleic-rich.

As a result of the extensive studies of the Liverpool school[2,4,5,6,7,8], the following facts emerge: The technical value of non-conjugated drying oils depends on their contents of linolenic and linoleic acid, and on the way in which these acids are combined in the mixed glycerides of the oils. A good drying oil must contain *at least* two polyethenoid acid groups in practically all its glyceride molecules. For a *quick*-drying oil the presence of a definite proportion of linolenic acid is desirable. The total content of polyethenoid acids is an approximate measure of drying power and should not be less than about 65-70 per cent[2]. To be equivalent in drying power to a good linseed oil a linolenic-rich oil should contain at least 60 per cent di- and tri-linolenic glycerides and at least 80 per cent di- and tri-polyethenoid glycerides (including 25 per cent tripolyethenoid). All glycerides should contain one linolenic acid group. For replacement of linseed oil a linolenic-rich drying oil should contain in its mixed fatty acids not less than 70 per cent (linolenic+linoleic) drying fatty acids, of which linolenic acid should form at least 50 per cent of the total fatty acids[6]. The suitability of a linoleic-rich oil so far as its use in paints is concerned is that it should contain not less than 67 per cent linoleic acid in its total fatty acids; it must consist of glycerides, 90 per cent of which should contain two or three linoleic groups in each triglyceride molecule, *i.e.*, it must not contain more than 10 per cent mono-linoleic glycerides[6]. All linoleic-rich oils which contain the requisite 67 per cent or more linoleic acid in their total acids are identical materials and completely interchangeable for technical purposes irrespective of agricultural origin (always provided, of course, that unduly large amounts of anti-oxidant or natural plant pigment do not interfere[8]). This last statement is of considerable importance, since it emphasises the importance of recognising the chemical status of natural drying oils rather than botanical origin.

One of the important findings of Hilditch's work was that natural drying oils conformed very closely with the *rule of even distribution*. Barker and Hilditch[5] examined the component glycerides of a number of linoleic-rich oils (Niger seed, safflower seed and six sunflower seed oils of differing linoleic acid content). Their results show that at 70 per cent linoleic acid content the proportions of di-linoleo glycerides reaches a maximum (about 90 per cent). No trilinolein

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is present until linoleic acid forms about 60 per cent of the total acids. The glyceride structure of these oils approximates to the even-distribution type.

Dutton and Cannon[9] claim, from studies of glyceride constitution by the countercurrent distribution method, that linseed oil conforms to the random distribution pattern. They isolated about 18 per cent of trilinolenin from linseed oil, a glyceride not permitted under the strict even-distribution pattern. Scholfield and Hicks[10] have used a similar technique to study the glyceride composition of soya-bean oil, and here again the random-distribution pattern is proposed. Further studies of this type may throw more light on the problem of distribution in glyceride oils which contain polyethenoid acids of differing unsaturation (where both linolenic and linoleic acids are present in quantity).

Segregation

The upgrading of drying oils by solvent segregation has received some attention in recent years. The furfural process of the Pittsburgh Plate Glass Co. and the liquid propane (*Solexol*) process of the M.W. Kellogg Co. are both operated commercially, the former mainly on soya-bean oil and the latter on fish oils and sunflower-seed oil. Both are countercurrent extraction processes carried out in packed towers. The furfural process has been discussed in detail by Gloyer[11]. Examples cited included the segregation of linseed oil of iodine value 180 into an extract (75 per cent) of iodine value 196 and a raffinate (25 per cent) of iodine value 132, and of soya-bean oil of iodine value 138 into fractions of iodine value 152 (60 per cent) and iodine value 118 (40 per cent).

The Solexol process as operated in South Africa has been described by Le Riche and Stubbs[12] with reference to the up-grading of sunflower seed and fish (pilchard) oils. Before enlarging on this particular subject it must be emphasised that any segregation process results in at least two fractions, and, if the non-drying low-iodine-value fraction does not command a premium over the original oil, the whole of the segregation cost must be borne by the drying fraction. Jordan *et al.*[13] have discussed the case for the installation of a solvent-fractionating plant in the U.K. and consider that, although the furfural process used for soya-bean oil fractionation in the U.S.A. could be used for up-grading *linolenic* oils, such as rubber seed and candlenut oil, up-grading of *linoleic* oils such as tobacco, sunflower and safflower would probably necessitate some plant modifications. The natural even distribution of the fatty acids in the glycerides of drying or semi-drying oils sets a definite limit to what can be achieved by solvent segregation. Le Riche and Stubbs have discussed the propane segregation of sunflower-seed oils varying from 40-70 per cent linoleic acid, and have shown that, if a target of 67 per cent linoleic acid is set for the *drying* segregate, only very small yields are obtained for those oils containing less than 60 per cent linoleic acid, *e.g.*, only 15 per cent of a fraction containing 67 per cent linoleic acid can be obtained from a sunflower seed oil of 56.3 per cent linoleic acid content. The parcels of segregated soya-bean oil examined in the author's laboratory some years ago did not live up to claims that the oil was an excellent substitute for linseed oil. Only by extension with 25 per cent of tung oil did it approach linseed oil in drying properties. The component fatty-acid analysis for the segregated oil is very different from that of a low-iodine-value linseed oil (only 15 per cent linolenic acid as compared

with about 55 per cent in linseed oil[14]). It was perhaps unfortunate that the segregated soya oils should have been described as a replacement for linseed oil. In the past, arguments for and against the installation of solvent-segregation plant in the U.K. have been influenced by economic factors—mainly price and availability of drying oils, considered together with the high capital cost of the plant itself. There is, however, a technical aspect of the subject, a study of which may bring about a renewed interest in segregation techniques in the not too distant future. Now that the importance of the chemical rather than the botanical status of natural glyceride oils is becoming recognised, and with the new knowledge on the constitution of drying oils, the industry should be better equipped to tackle problems relating to the choice of oil component for a particular film-forming medium. In choosing the oil component of a paint medium, whether it is to be modified as, for example, by alkyd formation, or processed by oxidation or thermal treatment, it should be known what is the ideal combination of glyceride molecules containing no, one, two, or three reactive (polyethenoid) acids which will *contribute* to a film with good physical properties, without at the same time leaving appreciable amounts of polyunsaturated centres in the film which can only undergo oxidative degradation. Attention may be drawn to a paper by Lundberg[15] who has stressed the need for research on the influence of glyceride composition on film-forming properties. Once information on this aspect becomes available, the whole question of solvent fractionation may well have to be considered in a new light.

Linseed, Tobacco Seed and Soya Bean Oils

It is appropriate to discuss some constitutive aspects of linseed, tobacco-seed, and soya-bean oils, since the first named is the principal drying oil, and the last two are in considerable use, particularly for alkyd-resin manufacture where their non-yellowing characteristics can be used to advantage. With both semi-drying oils it is important to realise that there can be considerable variations between various parcels of oil. Table II gives some idea of the extreme variation.

TABLE II

VARIABILITY OF SEMI-DRYING OILS

Content of	Tobacco seed (%)	Soya Bean (%)
Saturated acids	10-15	12-14
Oleic	15-30	22-34
Linoleic..	55-75	50-66
Linolenic	trace	2-9
Iodine value	135-147	103-152

It will be appreciated that in alkyd-resin manufacture there are factors influencing drying and film properties other than chemical constitution of the modifying oil, *e.g.*, oil length, polyalcohol used, degree of condensation

and polymerisation, and whether some modification such as styrenation or maleinisation is used. Nevertheless it should be appreciated that variations in fatty-acid composition of semi-drying oils may lead to variations in drying and yellowing of the film. In the formation of long-oil alkyds it is important to consider whether the oil component has the necessary 65-70 per cent drying fatty acids in its glycerides. In some notes on non-yellowing oils, Greaves[16] has stated that a linoleic acid content of 70 per cent or over should be guaranteed, as well as some greater constancy in composition, if there is to be an increased and sustained interest in tobacco-seed oil as a drying oil.

Even linseed oil, the principal drying oil, is subject to considerable variation as between different parcels. Agricultural factors such as climate and environment in seed development are responsible for the differences. Painter[17] has stated that adverse climatic conditions, high temperature and insufficient moisture while the seed ripens, are factors sometimes responsible for the production of low-iodine-value linseed oil. The B.S. Specification for linseed oil does not include a clause describing linseed oil in terms of fatty acid composition. In addition to such identification tests as saponification value, refractive index, unsaponifiables, etc., it states that the iodine value shall not be less than 175. There is not much the oil processor can do about variations between parcels of oil and economic factors do not enable him to supply, on request, oils to a close specification with regard to iodine value.

Since the importance of recognising the chemical rather than the botanical status of technical oils has been discussed, it would seem appropriate to consider the chemical constitution of various linseed oils with reference to some recently published work. Pouchon and Massoni[18] have examined a large number of linseed oils from different sources. Their results indicate that the same quality of a seed cultivated in the same country can yield oils of different composition depending on climatic conditions. These workers collected data from 300 different linseed oils, and plotted the content of linolenic, linoleic, oleic and saturated acids against the iodine value. One can obtain an idea of the composition of linseed oil of a known iodine value from these curves, which are a fair average, but to get the true composition of an oil it is necessary to carry out the analysis in the usual way. Fig. 1 shows the relation between composition and iodine value, based on the data of Pouchon and Massoni. It indicates the following trends for oils of iodine value 175-200: An almost linear increase of linolenic acid from 48-61 per cent with increase in iodine value, an almost constant content of linoleic acid (*ca.* 14 per cent) with increasing I.V., a slow decrease of oleic acid content from 25 to 20 per cent, and a decrease of saturated acids from 11 to 6 per cent.

Recently Fauve[19] carried out an investigation in which he compared linseed oils of low and high iodine value, in stand-oil and alkyd-resin manufacture, and in the drying and yellowing of white paints based on these oils. He concluded

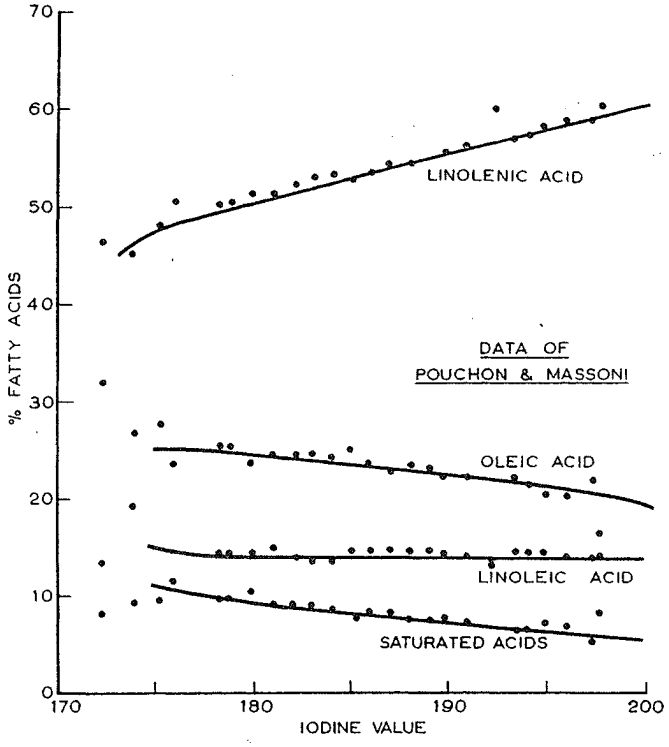


FIG. 1. VARIATION OF COMPOSITION OF LINSEED OILS WITH IODINE VALUE
[*By courtesy of Peintures, Pigments, Vernis*]

that high-iodine-value oils of high linolenic acid content polymerised more rapidly in stand oil manufacture than oils of low iodine value (and hence lower linolenic acid content). Long-oil glycerol alkyds based on low-iodine-value oils bodied slower and were slower drying than those based on high-iodine-value linseed oils. In rather shorter oil alkyds, high-iodine-value oils gave rise to a more serious risk of gelation. Comparing linseed oils refined and bleached to the same degree, the high-iodine-value oils yellowed more than oils of lower unsaturation. (In this work Fauve took particular care to compare oils from which impurities, such as phosphatides and anti-oxidants, had been removed by careful refining and which had been stored out of contact with air and light prior to their use.) He concluded that the yellowing, drying and reactivity of an oil was closely related to the iodine value, itself a function of density and refractive index.

Fauve emphasised the importance of accuracy of measurement in determining the physical and chemical constants of linseed oil. In relating iodine value to the refractive index and density of an oil, he pointed out that measurements must be made on properly refined pure oils. (Oils stored in contact with air which have undergone oxidation, will have an increased refractive index

(R.I.), lower iodine value (I.V.), and perhaps increased viscosity.) He referred to several expressions relating I.V. with R.I., and I.V. with density of the oil. Fauve's own expression is: $I.V.=(n_D^{20}-1.4626)\times 10^4$.

Hence, an oil having an R.I. at 20°C of 1.4815 will have an I.V. of $(1.4815-1.4626)\times 10{,}000=189.0$.

His expression relating density (ρ) at 20°C with I.V. is: $I.V.=(0.6733\rho-0.60658)\times 10^4$.

In determinations of the R.I. it is essential to have an accurate refractometer and constant temperature conditions. In the author's laboratories it has been found that for freshly refined and bleached linseed, tobacco-seed and soya-bean oils, the I.V. is related to the refractive index by the expression:

$$I.V. = (n_D^{25} - 1.4570) \,/\, 0.00012$$

The above expression agrees quite closely with the experimental findings of Zeleny and co-workers[20], who state that with linseed and soya-bean oils the following relationship between I.V. and R.I. at 25°C holds:

$$I.V. = (n_D^{25} - 1.45765) \,/\, 0.0001164$$

The refractive index, if determined accurately, constitutes a useful sorting test on oil deliveries, since it can be carried out much more rapidly than the iodine value determination.

In this paper attention has been drawn to some of the important results of investigations of the chemical constitution of drying oils. A good deal remains to be done, and perhaps one of the widest gaps in knowledge concerns the chemistry of the non-glyceridic components of technical glyceride oils. The part played by the natural pigments, trace metals, and anti-oxidants in the processes of autoxidation has attracted the attention of chemists in the edible oil industry, and is a field which should be investigated more fully by technologists in the surface-coatings industry.

Thermal Polymerisation of Drying Oils

Many investigations of the mechanisms of thermal polymerisation and autoxidation have been carried out in recent years. In this country many important contributions have come from the Paint Research Station, and research has been active abroad, particularly in the U.S.A. At the beginning of the paper, the polyester concept of drying-oil polymerisation was referred to, and it is appropriate to refer to it again before discussing some recent advances in the knowledge of the chemistry of thermal polymerisation. Only a relatively short time ago it was thought that stand oils were made up largely of dimer and trimer glyceride polymers, and contained no higher polymer than tetramer. This was based on number-average molecular-weight measurements, which for stand oils yield values of the order of 3000. More attention is now being given to weight-average molecular-weight determinations, which take into account the presence of large polymers. It is known that stand oils are extremely heterogeneous and contain a range of molecular species varying from very high to very low molecular weight polymers, as well as monomeric unreacted glycerides. For example, a linseed stand oil with a viscosity as low as 20 poise at 25°C may contain fractions of molecular weight of 120,000 or more. Hoeve and Sutton[21,22] have shown, with slow-bodying

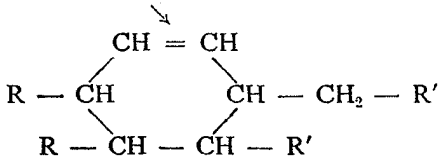
oils such as linseed oil, that, provided the various acids are randomly esterified with the alcohol groups in the various glycerides, Flory's theory of polycondensation reactions can be applied, enabling changes in molecular-weight distribution to be followed as polymerisation proceeds. Also the relationship between the distribution and the viscosity can be studied. Studies of this kind involve determinations of the amount of mono-, di- and tri-basic units in the polymerised oils (determined by methanolysis of the polymerised oil followed by molecular distillation of the methyl esters so as to segregate the monomeric, dimeric and trimeric acid units). Having obtained these data, the amounts of monomeric glycerides and various polymeric glyceride species can be calculated using Stockmayer's equations[23]. In this way Hoeve[22] has shown that a linseed stand oil polymerised for 6 hours at 300°C contains appreciable amounts of glyceride polymer with a molecular weight higher than pentamer (*i.e.*, five interlinked glyceride units). There is no doubt that fundamental studies of this kind are of practical importance. They might also be applied to changes in molecular-weight distribution during the drying of an oil film, in which case it might be possible to investigate drying and mechanical properties as a function of molecular-weight distribution.

Mechanisms of Thermal Polymerisation

The precise mechanisms by which addition polymerisation of unsaturated fatty acid chains takes place has been the subject of considerable research and discussion. With conjugated esters such as tung or oiticica oil it has been established that dimerisation takes place between a double bond on one chain and a conjugated diene on another, uniting the chains by a six-membered cyclic group (Diels-Alder mechanism). Chemical evidence for the existence of a six-membered ring substituted in four neighbouring positions in the dimer of methyl β-elaeostearate has been obtained by Clingman *et al.*[24]. On substitutive bromination followed by dehydrobromination and then oxidation, the dimer yields prehnitic acid (1 : 2 : 3 : 4-benzene tetracarboxylic acid). It has been generally accepted that dimerisation of non-conjugated drying-oil esters proceeds first by conjugation of the double bonds in a linoleate or linolenate radicle. Two such radicles can dimerise by a Diels-Alder reaction. Addition can also occur between an isolated double bond on a non-conjugated radicle and the conjugated diene group in an isomerised linolenate or linoleate radicle.

$$R-CH=CH-CH_2-CH=CH-R' \xrightarrow[\text{conjugation}]{} R-CH=CH-CH=CH-CH_2-R'$$

$$R-CH=CH-CH=CH-CH_2-R' + R-CH=CH-R'$$



Evidence for this mechanism has been provided by Waterman and co-workers[25] using refractive-index methods with polymerised drying oils (tung, linseed and poppyseed), but there has been no conclusive chemical evidence that it is the sole operative mechanism. It is possibly significant that Clingman *et al.*[24] could obtain only very low yields of prehnitic acid when they applied the bromination, dehydrobromination, and oxidation sequence to the dimers of methyl linoleate and linolenate. A most important contribution has been made by Rushman and Simpson[26], who carried out a kinetic study of the dimerisation and conjugation reactions in the heat polymerisation of methyl linoleate. These workers have shown that polymerisation is not necessarily preceded by a conjugation step. Both conjugation and dimerisation follow second-order kinetics, and the dimers and conjugated isomers are formed by the reaction of free radicles according to the following reaction scheme:

$$\underset{\text{(first chain)}}{CH_3[CH_2]_4 - CH = CH - CH_2 - CH = CH - [CH_2]_7 - COOCH_3} + \underset{\text{(second chain)}}{CH_3[CH_2]_4 - CH = CH - CH_2 - CH = CH - [CH_2]_7 - COOCH_3}$$

Abstraction of hydrogen atom from and active methylene group on the first linoleate chain gives the free radicle, R_1:

$$CH_3[CH_2]_4 - CH = CH - \dot{C}H - CH = CH - [CH_2]_7 - COOCH_3$$

Transfer of a hydrogen atom to a double bond in the second linoleate chain gives the free radicle, R_2:

$$CH_3[CH_2]_4 - CH_2 - \dot{C}H - CH_2 - CH = CH - [CH_2]_7 - COOCH_3$$

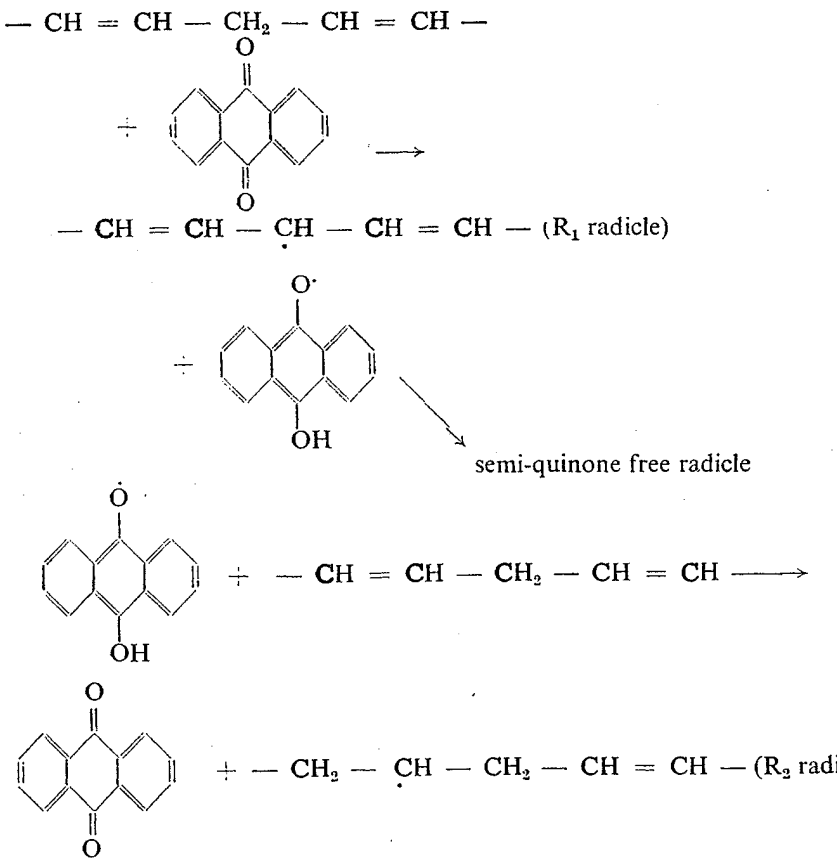
The radicle R_1 is a resonance hybrid which can be represented in the three limiting forms:

$$\begin{cases} CH_3[CH_2]_4 - CH = CH - CH = CH - \dot{C}H - [CH_2]_7 \cdot COOCH_3 & \text{(I)} \\ CH_3[CH_2]_4 - \dot{C}H - CH = CH - CH = CH - [CH_2]_7 \cdot COOCH_3 & \text{(II)} \\ CH_3[CH_2]_4 - CH = CH - \dot{C}H - CH = CH - [CH_2]_7\ COOCH_3 & \text{(III)} \end{cases}$$

If a reversal of the hydrogen-transfer reaction occurs, the products of the reversal step will depend on which resonance structure is involved. (I) and (II) will produce conjugated linoleate isomers, while (III) will regenerate a normal linoleate molecule. Combination of R_1 and R_2 radicles leads to dimer formation.

The free-radicle hypothesis of Rushman and Simpson furnishes an explanation of the behaviour of quinone-type catalysts in stand oil manufacture, *e.g.*, anthraquinone. The most suitable catalyst in the free-radicle reaction would be one which could offer a low energy path to the formation of R_1 and R_2 radicles. Anthraquinone is easily reduced and it is postulated that, in the catalysis of the free-radicle process, the first step is abstraction of a hydrogen atom from an active methylene group in a linoleate chain to produce an R_1 radicle and a semi-quinone-type free radicle. The latter acts as an intermediate

carrier of the hydrogen atom and in the second step donates this hydrogen atom to another normal linoleate chain to produce an R_2 radicle. The catalyst forms a readily reversible oxidation reduction system.



Rushman and Simpson have in fact shown that low concentrations (0.5 per cent) of the quinone catalyse both dimerisation and conjugation. Concentrations above 0.5 per cent do not appear to catalyse dimerisation, but under these conditions the relationship between catalyst concentration and conjugation is almost linear.

The free-radicle polymerisation of methyl linoleate does not preclude dimerisation between conjugated isomers, by, for example, a Diels-Alder addition mechanism, but indicates that the bulk of dimer is formed by *direct* dimerisation of the linoleate chains. Although the precise mechanisms of thermal polymerisation have not been established with certainty in the case of non-conjugated drying oils, the present state of knowledge perhaps indicates that both mechanisms (free radicle and Diels-Alder addition) are operative.

Inter- and Intramolecular Polymerisation

In the polymerisation of drying oils the main reaction is one of dimerisation between unsaturated fatty acid chains on separate triglyceride molecules (interpolymerisation). A relatively small amount of intrapolymerisation (between fatty acid chains on the same triglyceride molecule) takes place in the early stages of the heat polymerisation[27]. There is also some evidence that some intra-acyl cyclisation also takes place during the heat bodying of both conjugated and non-conjugated drying oils[28,29,30].

Interchange Reactions

Radioactive isotopes have been used at the Paint Research Station[31] to study interchange reactions such as occur in stand oil and varnish manufacture. Using esters of drying-oil acids it has been shown that all three types of reaction —acidolysis, alcoholysis, and trans-esterification—proceed at measurable rates at 300°C in the absence of catalysts; trans-esterification is slower than alcoholysis and acidolysis, and at 200°C no measurable trans-esterification occurs in the absence of catalysts, and at this temperature alcoholysis is faster than acidolysis. It is concluded that in most practical systems the rate of rearrangement for all types of reaction at temperatures around 300° will be sufficiently great to ensure a close approach to the equilibrium distribution.

Studies of the Rate of Polymerisation of Drying Oils

In calculating the rate of bodying of drying oils it is useful to adopt the K value measurement, which is the slope of the curve of log (viscosity) against time of bodying. Cannegieter[32] describes the straight line relationship between log (viscosity) and time, and calculates a polymerisation constant, K:

$$K = \frac{\log\eta_2 - \log\eta_1}{t_2 - t_1} \text{ at constant temperature}$$

where $\eta_{1,2}$ is the viscosity (poise) at time $t_{1,2}$ (min.).

Anderson and Porter[33] have found that on plotting log (viscosity) against time for various drying oil blends bodied at constant temperature the curves obtained are in three sections (between 0.5-100 poise at 25°C): a straight line of slope K_1, a straight line of slope K_2, and a third portion in curved form (of continuously increasing slope). These workers have plotted the overall values of K (*i.e.*, between 0.5-100 poise) for a number of polymerised drying and semi-drying oil blends against various functions of the component fatty acid analysis. They have shown that the function: 2.0 (per cent linolenic)+ 1.6 (per cent linoleic)+0.6 (per cent oleic), gives a figure which predicts the bodying rate (up to 100 poise) better than does the iodine value. In the author's laboratory curves similar to those of Anderson and Porter have been obtained in the relationship log (viscosity) (stoke) against time of polymerisation, following heat-bodying studies with drying and semi-drying oils. In a recent investigation[35] of the behaviour of various drying and semi-drying oils and mixtures of these oils (linseed, tobacco-seed, soya-bean) in the manufacture of long-oil pentaerythritol alkyds, the overall polymerisation constants have been calculated in the preparation of low-viscosity (1.0 stoke at 25°C) stand oils which have been used for the preparation of the alkyds. It has been found

that there is good correlation between the overall K value and the following function (F) of the fatty acid analysis[34]:

$$F = (4.5\ \text{Le} + 2.0\ \text{Lo})^2 / 1000$$

where Le = % linolenic acid, and

Lo = % linoleic acid

Rates of polymerisation have been determined at two reaction temperatures, 282°C and 240°C. and in both cases an almost linear relationship is obtained[35] between the K value and the function $(4.5\ \text{Le}+2.0\ \text{Lo})^2/1000$. An interesting feature of these experiments is the slow but measurable rate of polymerisation of the drying oils at 240°C (alkyd-making temperature). An estimate of the bodying rate of a non-conjugated drying oil can be obtained from a consideration of the component fatty acid composition.

Effects of Oxygen in the Heat Polymerisation of Drying Oils

In comparing the properties of open- and closed-pot stand oils, it is necessary to take into account the manufacturing conditions, particularly for the open-pot stand oils. Access of air (oxygen) has the effect of accelerating the rate of bodying to an extent depending on a number of factors, such as mass of oil, area of surface exposed to air, and degree of agitation of the oil. An investigation has been carried out in the author's laboratory in an attempt to determine the effects of oxygen on the heat polymerisation of linseed oil refined to varying degrees. In the apparatus adopted for the experiments, a constant quantity of gas was passed over the surface of the oil during heat treatment, the oxygen content being varied for each experiment by diluting the gas with carbon dioxide. Although this work is still proceeding, the following relationship appears to hold:

$$K = K'\left(1 + \frac{A\rho\ \alpha\ p}{M}\right)$$

where: K = bodying rate of drying oil processed under gas stream with oxygen of partial pressure p atmospheres,

K' = bodying rate of the same drying oil processed out of contact with air (*i.e.*, where $p=0$),

A = area of surface exposed to gas stream (cm.^{2}),

α = a constant, the value of which depends on the shape of the vessel and whether stirring is used,

M = mass of oil (grams), and

ρ = density of oil (g./cm.^{3}).

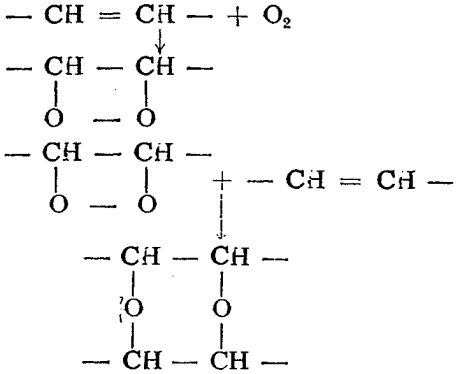
For a cylindrical vessel the expression becomes:

$$K = K'\left(1 + \frac{\alpha\ p}{L}\right)$$

where: L = depth of oil in vessel in cm. This follows since $\frac{M}{\rho}$ = volume and $\frac{A}{\text{volume}} = \frac{1}{L}$.

Autoxidation of Drying Oils

Considerable advances have been made in our knowledge of the autoxidation of drying oils. Not many years ago classical theory held that oxidation occurred at the double bonds in both non-conjugated and conjugated drying oils, leading to the production of cyclic peroxides, which could further react to form various types of oxygen-containing rings between chains:



The work of Farmer and his associates[36] first demonstrated that oxidation occurs at an active methylene group with the formation of a hydroperoxide, the initial unsaturation of the fatty acid chain (linoleate, linolenate) remaining unchanged in the primary oxidation stage. The oxidation is a free-radicle chain reaction and takes place according to the following scheme:

RH = linoleate or linolenate chain (H is a hydrogen of the active methylene group).

Initiation: $RH \rightarrow \dot{R} + H$
(promoted by U.V. light or metal catalysis and traces of peroxides)

Propagation: $\dot{R} + O_2 \rightarrow \dot{R}O_2$

$\dot{R}O_2 + RH \rightarrow ROOH + \dot{R}$ (considerable conjugated hydroperoxide is formed as a result of resonance).

Termination: $2\,\dot{R}O_2 \rightarrow R - O - O - R + O_2$

$\dot{R} + \dot{R} \rightarrow R - R$

$\dot{R}O_2 + \dot{R} \rightarrow R - O - O - R$

Decomposition of hydroperoxides (thermal):

$$ROOH \xrightarrow[\text{or action of driers}]{\text{heat } 100^\circ C} \dot{R}O + \dot{O}H$$

radicle attack on unchanged linoleate and linolenate.

$\dot{R}O + RH \longrightarrow ROH + \dot{R}$

$\dot{O}H + RH \longrightarrow \dot{R} + H_2O$

Dimerisation: $\dot{R} + \dot{R} \longrightarrow R - R$ (carbon—carbon linked dimeride)

$\dot{R} + \dot{R}O \longrightarrow R - O - R$ (ether linked dimeride)

In the particular case of linoleic acid oxidation the reaction would proceed according to the following scheme:

$$
\begin{array}{ll}
 & -CH=CH-CH_2-CH=CH- \\
 & \downarrow (-H) \\
[\dot{R} + O_2] & -CH=CH-\dot{C}H-CH=CH- \\
\downarrow & + O_2 \\
 & \downarrow \\
[\dot{R}O_2] & -CH=CH-CH(O-O\cdot)-CH=CH- \\
[\dot{R}O_2 + RH] & -CH=CH-CH(O-O\cdot)-CH=CH- \\
 & + \\
 & -CH=CH-CH_2-CH=CH- \\
 & \downarrow \\
[ROOH + \dot{R}] & -CH=CH-CH(O-OH)-CH=CH- \\
 & + -CH=CH-\dot{C}H-CH=CH-
\end{array}
$$

A considerable amount of the hydroperoxide formed will be conjugated due to double-bond shift as a result of allylic resonance.

$$-CH(O-OH)-CH=CH-CH=CH-CH=CH-$$

Decomposition of hydroperoxide:

$$ROOH \rightarrow \dot{R}O + \dot{O}H$$

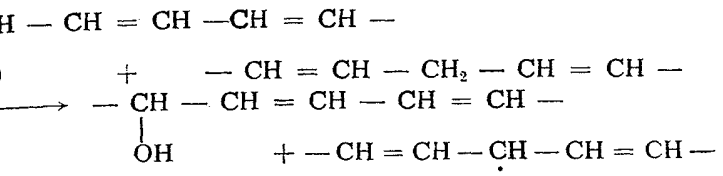
e.g., $-CH(O\cdot)-CH=CH-CH=CH-CH=CH- + \dot{O}H$

Radicle attack on monomer:

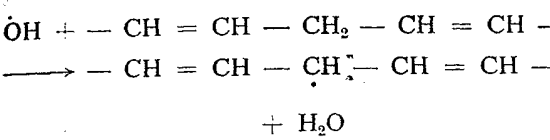
1. $\dot{R}O + RH \rightarrow ROH + \dot{R}$

2. $\dot{O}H + RH \rightarrow \dot{R} + H_2O$

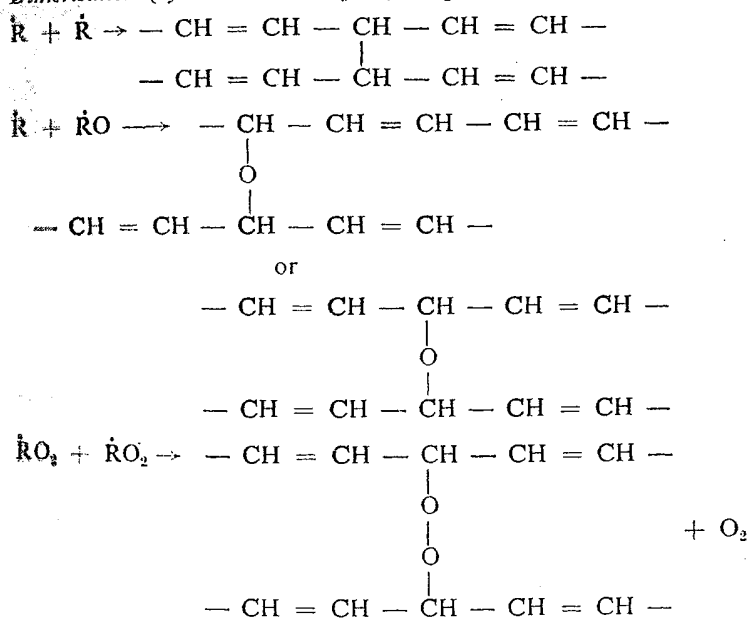
i.e., 1.



2.

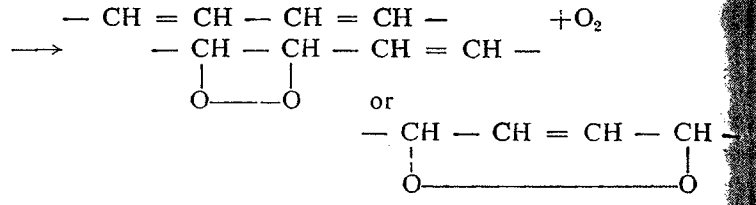


Dimerisation (*by combination of* $\dot{R}$, $\dot{R}O_2$, $\dot{R}O$, *etc.*):



The conjugated systems in the dimers or hydroxylated monomers may undergo further oxidation or attack by free radicles, the further attack on the dimers resulting in cross-linking of glycerides during the drying of paint media. The oxidation of conjugated systems does not appear to involve production

of hydroperoxides, but some cyclic peroxides are formed by 1 : 2 or 1 : 4 addition.



Most of the polymer formed from the oxidation of conjugated esters appears to be carbon–carbon linked, the high molecular weight of the polymeric portion suggesting that a chain mechanism is operative. The mechanisms by which conjugated species polymerise in the autoxidation of drying oils requires further study, and presents one of the gaps in our knowledge of the mechanism of film formation. It is certain, however, that an oil film during drying is an extremely dynamic system involving the reactions of free radicles in the building up of a macromolecular structure.

Catalysis of Autoxidation

It is generally understood that the action of those driers that exist in two valency states, *e.g.*, cobalt and manganese, is to decompose the hydroperoxides which are formed in the primary stage of autoxidation, at temperatures normally associated with drying. In the decomposition of hydroperoxides, these metals are oxidised from the lower to the higher valency state.

$$Co^{\cdot\cdot} + ROOH \rightarrow Co^{\cdot\cdot\cdot} + \dot{R}O + \bar{O}H$$

or $\bar{R}O + \dot{O}H$

$$Co^{\cdot\cdot\cdot} + R\bar{O} \rightarrow Co^{\cdot\cdot} + \dot{R}O$$

$$Co^{\cdot\cdot\cdot} + \bar{O}H \rightarrow Co^{\cdot\cdot} + \dot{O}H$$

The $\dot{R}O$ and $\dot{O}H$ radicles then attack unchanged unsaturated fatty acid chains at the reactive methylene groups as already described.

The oxidation of cobalt from the divalent to the trivalent state by drying oil peroxides is used as a preliminary sorting test in the author's laboratory to assess the extent of oxidation of drying oils during storage. Some time ago it was found[37] that alkali-refined linseed oil of high peroxide value, when used for alkyd-resin manufacture, gave rather dark alkyds which also polymerised at an abnormal rate during their manufacture. It has now been found that, by shaking up equal volumes of a refined and bleached linseed oil and a solution of cobalt naphthenate (0.001 g. Co per ml.) in White Spirit, the extent of oxidation in terms of peroxide oxygen can be assessed approximately by the development of colour from violet to green. A colorimetric method is used which relates Lovibond colour in red, yellow and blue units with the peroxide value in mg.-equiv. O_2 per kg. oil. This test *alone* does not give an idea of the previous history of the refined oil. For example, the peroxide value may have decreased from a fairly high value following decomposition of

hydroperoxides. In conjunction with the cobalt drier test, a test is made for the detection of decomposition products in the oil—rather on the lines of the Kreis test for rancidity. Palumbo[88] has devised a test to differentiate between oils which have undergone oxidation during thermal treatment and those which have not. It is a colorimetric test for aldehydes: 20 ml. of oil are treated successively with 10 ml. of a 1 per cent solution of alcoholic phloroglucinol and 10 ml. of concentrated hydrochloric acid. The development of a pink colour in the aqueous layer denotes the presence of aldehydic decomposition products.

Table III illustrates the application of the cobalt-drier and phloroglucinol tests. Two samples (500 g. each) of alkali-refined bleached linseed oil were stored in open porcelain dishes for 16 months at room temperature. To one sample (B) was added 0.1 per cent di-*tert.*-butyl hydroquinone before storage. Sample A was untreated.

TABLE III

COLOUR REACTIONS

Cobalt Drier Solution

	A	B
After six weeks' storage ..	Green	Pink
After three months' storage ..	Deep Green	Pale Yellow
After eleven months' storage..	Deep Green	Yellow-brown

Phloroglucinol Test

	A	B
After six weeks' storage ..	Cherry Red	Pale Pink

After eleven months Oil A had skinned over and had bleached considerably, whereas Oil B had not skinned and had substantially the same colour as the fresh oil. On heating Oil A to stand-oil making temperature, it darkened considerably (typical of highly oxidised oils); Oil B was bleached on heat treatment.

CONCLUSIONS

No attempt has been made to review past developments in the various fields of modified drying oils, *e.g.*, styrenated oils, epoxidised oils, isomerised oils, maleinised oils, etc. Research has been active in these fields, as reference to the published literature will show. More recent developments such as the new unsaponifiable drying oils from fatty acids will no doubt receive considerable attention in the future, and there is likely to be increased interest in the use of drying oils as raw materials, both for the preparation of chemical intermediates, and for new and improved surface-coating media. The object of this paper has been to show how much industry has come to depend on fundamental research for a better understanding of drying oil media. A great deal of progress has been made in the past twelve years or so, and with new knowledge on the chemistry of drying oils at our disposal, industry should be better equipped to tackle the many unsolved problems in its technology.

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[*Received* 23 *October* 1957