possesses and also adds to the good flow-characteristics of the finished ink.

The importance of good flow and spreading on a tin panel can be more fully appreciated if one realizes that excellent ink coverage is expected in offset printing with unbelievably thin films of ink. Offset printing often deposits ink films in the neighborhood of .0001 in.

Over-Print Varnishes

O.P. varnishes find themselves occupying a larger and larger niche in the over-all scheme of printing-ink vehicles. O.P. varnishes serve a very definite function, a function which is dual in nature. Such products as catalogs, magazines, cartons, etc., which are handled considerably and are subject to soiling can be protected by the application of an O.P. varnish. At the same time these products are made more attractive by the increased luster and brilliance imparted to them by the over-printing process. True the printer would like to obtain these results with straight inks but often, to gain specific results he desires such as fast dry, toughness, and flexibility, he must formulate so as to suffer loss of gloss.

Over-print varnishes are complicated mixtures containing drying oils, resins, waxes, solvents, driers, greasy lubricants, and sometimes corn starch. Initial color and color retention should be given uppermost consideration when one attempts to formulate an oil-based O.P. varnish.

Oils are selected on the basis of their color-retaining properties, speed of dry, hardness, gloss, and scuff-resistance qualities. The resins used are selected for similar reasons, but in addition to these properties they must possess good solubility and wetting characteristics.

One other point of prime importance concerns varnish hold-out, that is, the ability of the printed and dried varnish to sit up high and glossy on the stock. Hold-out is a necessary and vital property for O.P. varnishes; without it you have no O.P. varnish. To achieve this, oil and resin must be so formulated or so cooked that the oil-resin combination yields a rather highly polymerized, viscous base. Of course, this can be carried too far and the O.P. base can be overpolymerized. In this case the solvent-thinned base will generally behave all right on low-speed presses but not high-speed presses. When an accident occurs on the latter, an umbrella and raincoat become standard equipment for the pressman because these overpolymerized, overcooked varnishes fly off the press faster than one can run for protection, and, in no time at all, everything in sight is coated with a heavy layer of varnish. If one is lucky, some varnish might be found on the stock.

What of the future? What type of oil vehicles will the printing-ink people need? As you can see, we need tough, scratch-resistant vehicles, fast-drying on the substrate but nondrying on the rollers of a press. Reduction of odor upon drying is another area where drying oils should be improved. These are just two areas that need improvement, and with constant work I am sure we shall see improvements brought about by cooperation of the printing ink manufacturers with the producers of drying oils.

Drying Oils in Floor Coverings

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IN ORDER to provide some background and perspective for discussion of the position of drying oils in resilient smooth-surface floor coverings, it may be helpful to review briefly the types of products, their relative production, and their use of raw materials. Resilient smooth-surface floor coverings may be arbitrarily divided into two categories, sheet goods and tile. Sheet goods are produced in rolls up to 90 ft. long and from 6 to 12 ft. wide. Tiles are produced, of course, in the familiar 9 x 9 in. and other sizes. Sheet goods may be subdivided into two categories, those based on drying oils, which are linoleum and felt base, and those based on resins of polyvinyl chloride and its copolymers. Linoleum is characterized by a wearing surface, up to ⅛-in. in thickness, in which the color and pattern are carried through to the backing. Felt base consists of a heavy coat of enamel paint, up to 6 mils thick, on a saturated felt backing. The service lives of the two products are proportional to the thickness of the wearing surface. Floorings based on polyvinyl chloride are similar in many properties to their drying oil counterparts; the principal difference, of course, is in the binder, which is a synthetic resin. In the "sheet vinyl" flooring the wearing surface is relatively thick, and the design is carried through to the backing. Synthetic resin counterparts of printed felt base are also available, where the vehicle is based on polyvinyl chloride and other resins instead of drying oils.

In the field of resilient tiles there is the familiar asphalt tile, based on binders having a bituminous derivation. Additional types are cork tile, rubber tile, linoleum tile, and tile based on resins of polyvinyl chloride and its copolymers.

The technology of resilient floor coverings has been described previously in the Journal of the American Oil Chemists' Society (1). There is also a very good article on the technology of floor coverings in the Encyclopedia of Chemical Technology by Kirk and Othmer under the subject of "Linoleum" (2). Generally speaking, all of these types are prepared from a drying oil or resinous binder, to which are added fillers and pigments to form a somewhat thermoplastic mix. This mix then is formed into flat sheets of various sizes by a variety of methods to produce either sheet goods or tile.

It would be appropriate now to discuss the statistics of the industry so as to provide some idea of the importance of each of these types of floor coverings and the usage of raw materials in each one. These statistics are accumulated by various branches of the federal government and are available in fairly good form up through about 1955. Since then there has been a distinct shrinkage in the number of producers so that

TABLE I
Production of Floor Coverings

	Total	Felt base	Asphalt tile	Linoleum and plastic	Rubber tile	Straight vinyl	Cork
1948[a]	3,653 × 10^6 ft.^{2}	2520 69%	400 11%	675 18.5%	58 1.6%	0	No data
1954[b]	3,660	2160 59	650 17.7	565 15.4	65 1.8	200 5.4%	20 .5%

[a] Source: N. Y. Journal of Commerce, quoted in Official Digest, 301, p. 105, 1950.
[b] Chemical and Engineering News, April 18, p. 1734, 1955.

TABLE II
Consumption of Raw Materials for Floor Coverings

	Total oil 000 lbs.[a]	Linseed[a]	% Linseed	Crude Tall[a]	% Tall	Polyvinyl chloride resins[b]
1948	166,471	109,861	66.8	E 10,000	6.0	
1949	142,975	76,037	53.2	14,552	10.2	
1950	149,809	90,098	60.2	15,107	10.1	
1951	132,244	101,004	76.2	13,929	10.5	
1952	125,032	89,184	71.4	12,221	9.8	....
1953	116,810	85,783	73.6	15,235	13.0	21,893
1954	112,750	72,655	64.6	25,750	22.8	34,890
1955	108,781	67,458	62.0	E 33,622	30.9	56,357
1956	100,452	51,437	49.	....	......	65,752
1957	70,318	32,678	46.5	....	......	81,248
1958	57,726	25,413	44.		......	113,584

[a] Source: U. S. Bureau of Census.
[b] Source: U. S. Tariff Commission.
E Estimates based on incomplete data.

it has not been possible to continue the statistics in the detail that was formerly available. However the trends in the past few years have not been greatly different from those of previous years so we may use the statistics for comparative purposes.

Table I shows the production of resilient floor coverings in the years 1948 and 1954. Felt-base production decreased from 69% of the yardage to 59%. Asphalt tile increased from 11% to nearly 18% whereas linoleum and plastic flooring declined from 18.5 to 15.5%. Rubber tile and cork tile represent small portions of the market. The polyvinyl chloride compositions have increased substantially, and the period shown, 1948 to 1954, represents what might be termed an induction period in the growth of this product. The next census was taken in 1958 and will be available next year. Table II shows the consumption of raw materials for floor coverings. In the first column are listed the total amount of drying oils. Until 1956 the usage of each major oil was published; since then only linseed has been listed, and this may be dropped. The figures show the considerable decline in the use of drying oils generally. Linseed oil itself held its share of the market, between 60 and 75% of the total, until 1956, when the percentage of usage declined markedly and has continued to do so. Tall oil usage rose moderately during the early 1950's, then more abruptly beginning in 1954.

It is probable that the rise in amount used has continued and that the percentage used has risen even more so. Figures since 1955 have not been made available. The increase in polyvinyl chloride resins, including copolymers, has risen sharply, as shown in the last column. The usage will probably be even larger for 1959, perhaps 140 million lbs. To summarize then, production of both linoleum and felt-base floor covering has declined very substantially, particularly felt base. The proportion of linseed oil in them remained fairly constant until three years ago, when it began to decline also, so there has been a distinct decrease in the amount of oil used. For the future we may expect the trends of the past to continue although the decline in the production of linoleum may be levelling off. It is possible that there may be a further sharp decrease in the production of felt-base goods made with drying oil composition as polyvinyl chloride resins are entering into this type of product also.

WE SHALL now proceed to a discussion of the polymer chemistry of oxidized drying oils, and it will be assumed that all of you have had at least a modest acquaintance with some of the general principles of polymer chemistry and that a brief review will suffice. First, and to my mind foremost, is the concept of functionality. A functional group is simply a potentially reactive position in a molecule. If we take equivalent amounts of ethylene glycol and adipic acid for esterification, we have a system whose average functionality is 2. There are, on the average, two functional groups per molecule, and we find that, after esterifying these materials to a low acid and hydroxyl number, we no longer have a simple definite compound but a mixture of compounds with a wide range of molecular weights. Separation of these into distinct molecular-weight species is exceedingly tedious. If the average functionality is greater than 2, such as can be achieved by adding glycerine or pentaerythritol in place of part of the glycol or by using a tribasic acid instead of the adipic acid, we shall find that instead of getting soluble, linear polymers we will get branched or cross-linked materials which gel and become insoluble before reaching a low acid number.

Proceeding then from this simple concept which has been very considerably expanded into complexities which need not concern us now, we may review briefly the factors which are important in polymer design, namely, chain length, attraction and fit of the chains. Generally speaking, the higher the molecular weight of a linear polymer, the longer will be the chains and the stronger will be the resin. The strength increases fairly sharply during the initial increase in length, but, after a certain chain-length has been reached, further increases in strength are relatively minor so that in most cases there is no great advantage in going to a chain length greatly beyond that which is adequate.

The concept of attraction between chains is an extremely interesting and complicated one. As you know, functional groups and other chemical structures have a certain degree of electrical polarity and

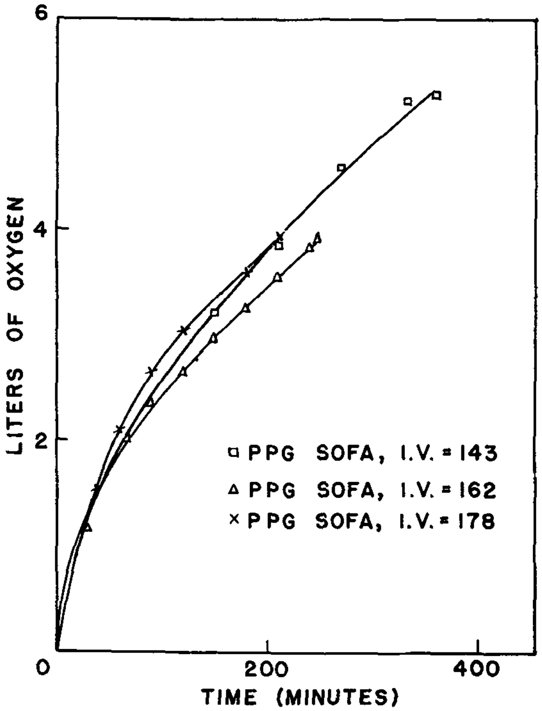

FIG. 1. Rate of oxygen absorption, glycerol esters of fractionated soybean oil fatty acids.

attract other groups which also have polar properties. These functional groups may be similar or not. Ether and hydroxyl groups are only slightly polar, ester groups somewhat more so, amide groups strongly so, isocyanate, nitrile, and nitro groups, very strongly so. A chain which incorporates a few of these groups will be more polar than a hydrocarbon chain. Both the polarity and the number of these groups in the chain will affect the attraction between the chains. The stronger the attraction between the chains, the stronger will be the polymer and the more nearly it will approach a cross-linked, three-dimensional structure.

A third factor is that of fit between the chains. If we have chains of regular, linear nature with few branches but with some polar groups along the chain, then the chains can fit well together and the maximum amount of advantage can be obtained from the polar groups present, affording a high degree of attraction between the chains. If, on the other hand, we wish to reduce the attraction between the chains, we can incorporate bulky or lengthy branches on the chains which will strongly interfere with the fit.

The next step is to apply these generalities to the practical drying-oil systems. First, of course, is the concept of functionality: what are the functional groups in a typical drying-oil system? Let us eliminate for a moment the complications introduced by alkyd technology and ignore the ester groups in the triglyceride oil. The functionality then depends directly upon the unsaturation, the number, type, and location of the double bonds. If we take linseed oil, for example, we find that it is composed of molecules which contain 0, 1, 2, or 3 double bonds in each of the fatty acid chains. It has been found by experience that an oleic acid chain with only one double bond is not particularly reactive toward oxidation or polymerization. Linoleic acid with two double bonds can be considered as having a functionality of one, that is to say, such a chain will react once with other similar chains. Linolenic acid with three double bonds has a functionality of about 1.5. If we have a triglyceride all of the acids of which are either saturated or oleic acids, it will not be particularly reactive. If we have one linoleic acid chain, the molecule as a whole will have a functionality of 1 and will react but it will not form much of a polymer. It is still not considered a drying oil. If however two of the chains have two double bonds, such as a dilinoleic glyceride, the molecule will have an average functionality of 2 and it can enter into a polymerization reaction with itself or with another drying oil molecule whose average functionality is 2 or more. If a substantial proportion of the oil consists of triglyceride molecules each of which has a high proportion of linolenic acid chains, the average functionality will be greater than 2 and cross-linked gels can be formed.

So far we have not discussed anything about the chemistry of the oxidation and polymerization reactions of drying oils. These are described elsewhere, and I shall not repeat except to say that the functionality concept is independent of the particular mechanism involved, whether it be oxidation or polymerization by heat bodying.

SINCE the bulk of drying oils used in the floor coverings are used in linoleum and in printed felt-base, the general chemical reactions of oxidation and polymerization can be applied to those processes. With reference first to linoleum, the traditional binder or cement is composed of a mixture of about three parts of drying oils and one part of rosin. These materials are charged to a large heated kettle, where air is vigorously mixed into intimate contact with the contents. The temperature ranges from 80–120°C., well below heat-bodying temperature, so that polymerization is predominantly of oxidized structures. The mixture absorbs a considerable amount of oxygen and becomes less soluble in nonpolar solvents such as hexane. Some of it eventually becomes insoluble even in polar solvents. The mixture also becomes gradually more viscous, indicating increasing molecular weight. In line with the usual concept of the oxidation of drying oils, the first reaction is the one with oxygen to form hydroperoxides. When driers are present, as they always are in commercial practice, the hydroperoxides do not accumulate but are immediately decomposed with the formation of the secondary products which are, for the most part, hydroxyl and carbonyl compounds. The decomposition of the hydroperoxides occurs by free radical mechanisms, during the course of which union of a number of the free radicals is possible to form dimeric, then polymeric materials of high oxygen content. There has been a good deal of speculation on the nature of the links between the chains in this oxidative polymerization, and we have found evidence that not all of the chains are similarly bound. Some of them appear to be linked through carbon-carbon bonds, others through ether-oxygen structures.

The importance of the rosin in the composition deserves a little attention. It acts as a so-called "peptizer" to delay the polymerization of the oxidized oil. It also inhibits the oxidation but is a still stronger inhibitor of the polymerization steps. The exact mechanism is not clear to us although it would appear to be a scavenger for certain types of free radicals. It itself undergoes a substantial amount of oxidation. About one-third of the rosin is chemically bonded with the drying oil by primary valence bonds through a free radical process. The rosin is not esterified during the process.

We may demonstrate the concept of functionality based on unsaturation in Figure 1, which illustrates the rate and amount of oxygen absorption of glycerol esters of soybean fatty acids. We have here esters of three grades of soybean fatty acids which were prepared by solvent extraction to have iodine values of 143, 162, and 178, respectively. The curves show that the ester with the lowest iodine value took the longest time to gel and in the process, of course, absorbed the most oxygen. This shows that a higher oxygen content, which requires a longer time to achieve, is necessary in order to build up the polymeric structure to the gel point. The middle curve is for the ester from the acids of 162 iodine value, which takes considerably less time to gel at a much lower oxygen content. The ester from the acids of 178 iodine value achieves about the same degree of oxidation but in a somewhat shorter time to gel. The same general principle is shown in Figure 2 with esters of soybean oil fatty acids. In this case the variation in functionality is achieved by the use of different polyols. The glycerol triester takes the longest time to gel and absorbs the most oxygen in so doing. The pentaerythritol tetraester gels much more quickly at a lower degree of oxidation. The tetramethylol cyclohexanol penta-ester gels in the shortest time at the lowest oxygen content. The comparative functionality of each ester is listed in Table III. For a direct comparison of cements themselves rather than synthetic esters, Figure 3 shows the oxygen content: time curves for linseed oil which gels fairly quickly at a moderate oxygen content, safflower oil which takes longer to gel and reaches a distinctly higher oxygen content, and soybean oil which takes considerably longer and achieves a slightly higher oxygen content. All the way through it is clear that an adequate degree of functionality in the molecule is necessary for polymerization to occur.

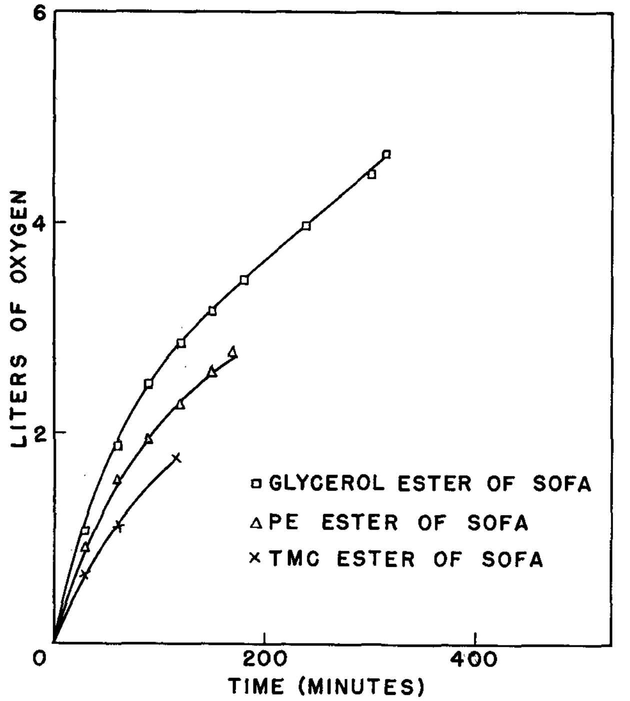

Fig. 2. Rate of oxygen absorption, esters of soybean oil fatty acids.

TABLE III
Functionality of Esters

	Ester	I.V.	f/chain	f/ester
Fig. 1	Glycerol-SOFA	143	.83	2.49
	Glycerol-SOFA	162	.94	2.82
	Glycerol-SOFA	178	1.04	3.12
Fig. 2	Glycerol-SOFA	129	.75	2.25
	P.E.-SOFA	123	.72	2.88
	TMC-SOFA	111	.65	2.92

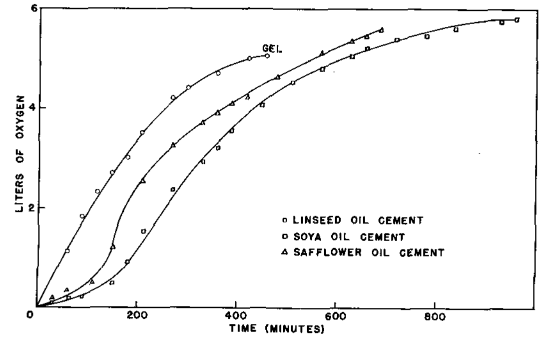

Fig. 3. Rate of oxygen absorption, linoleum binders.

The types of oxidation products which are formed during oxidation have been determined, and the relative amounts produced are shown in Figure 4. The dotted line is a measure of the total amount of oxygen retained. The curves are for each type of functionality, plotted against mols of oxygen per one-third mol of oil. The peroxide content rises, then levels off, as no driers were present. The carboxyl groups are produced in moderate amounts, and hydroxyl groups in larger amounts. We have also found appreciable quantities of oxirane and carbonyl oxygen. The total does not account for all the oxygen consumed by the oil, and it is believed that the remainder is present as ether oxygen, probably as a cross-link between chains.

In a quantitative oxidation in which all the oxygen consumed was measured and all the volatile products

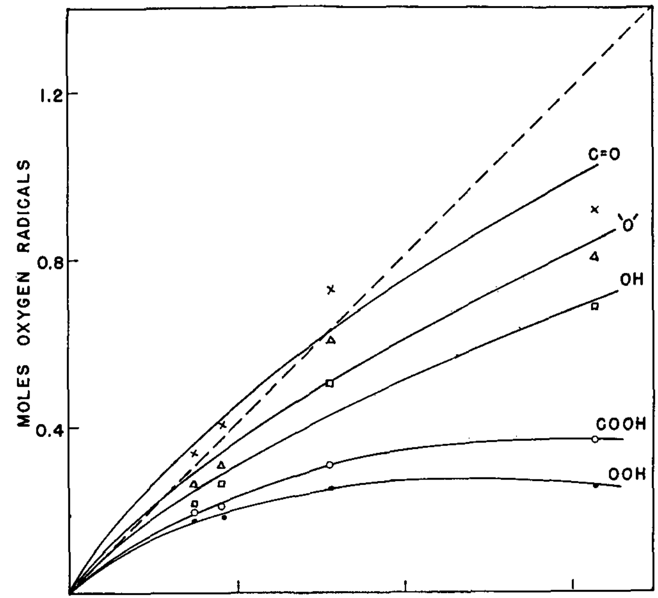

Fig. 4. Oxidation of linseed oil, 80°C.—formation of functional groups.

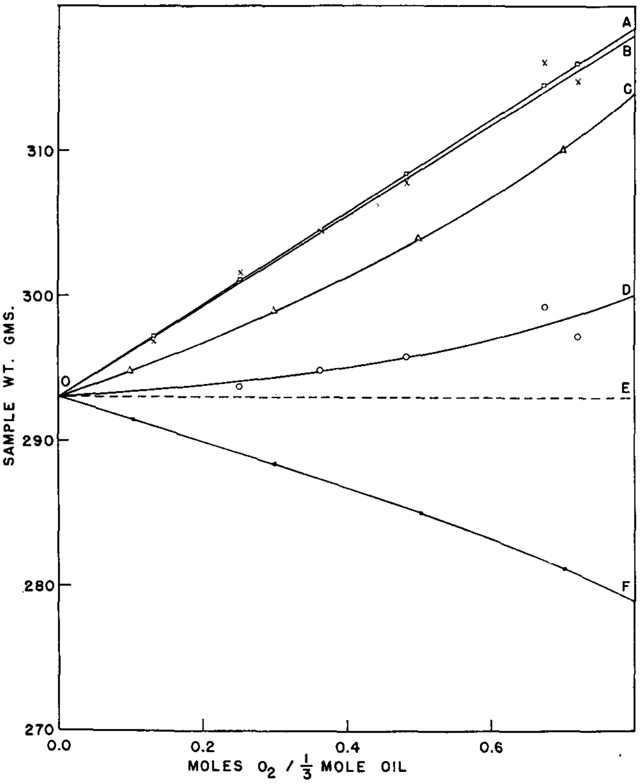

FIG. 5. Oxidation of linseed oil, 100°C.—material balance.

collected and analyzed as well as the residue, a material balance was obtained as shown in Figure 5. Sample weight in grams is plotted against mols of oxygen per one-third mol of oil. The original weight of sample was 293 g., about one-third gram molecular weight. The area AOE is total weight of oxygen consumed; DOE is the gain in sample weight (residue); DOF is the oxygen retained in the residue; EOF is the carbon and hydrogen lost by the oil; BOD is the weight of volatile collected, COD the carbon and hydrogen in the volatiles; BOC is the oxygen in the volatiles and AOB the amount of error.

From these data one may say that, under these oxidation conditions, approximately two-thirds of the oxygen consumed is retained in the residue, the rest is in the water and other volatiles. Initially all the oxygen consumed forms hydroperoxides. From model oxidation studies, in the presence of driers, the hydroperoxides decompose to form equal amounts of hydroxyl and carbonyl compounds. The hydroxyl material is fairly stable; the carbonyl seems to decompose or react further, and carboxyl, ester, and oxirane groups appear though not necessarily from the carbonyl material directly.

The course of oxidation can be followed also by extraction of the cement during the oxidation process. Figure 6 shows composition *versus* time of oxidation. To obtain these data, samples were withdrawn from the oxidizer at 4-hr. intervals and submitted to a liquid-liquid extraction analysis in a suitable small-scale apparatus. These samples were extracted first with refluxing hexane for 48 hrs., and both the residue and extract were dried and weighed. The residue was then extracted with refluxing ethyl ether for 24 hrs., and again the residue and extract were dried and weighed. In all cases close agreement was found between the weight of the extract and the loss in weight of the residues. The hexane extract consists primarily of unoxidized and unpolymerized components in which stearic and oleic fatty acid chains predominate. The ether extract consists principally of oxidized but unpolymerized compositions. The residue from the ether extraction is known as linoxyn and consists of oxidized and polymerized components.

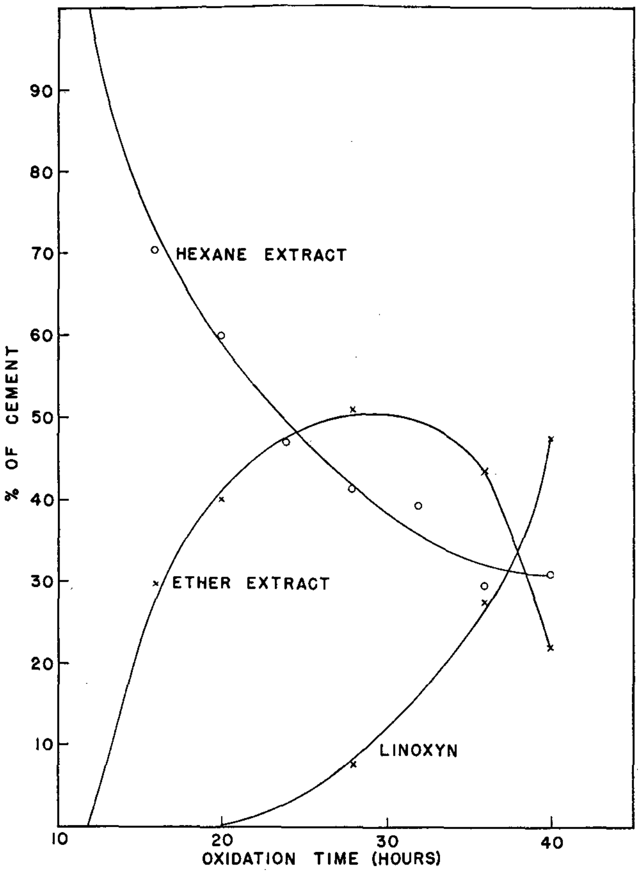

FIG. 6. Oxidation of linoleum binder—composition *vs.* oxidation time.

These curves are typical of consecutive reactions, where A reacts to form B, which in turn reacts to produce C. The intermediate B represents the ether extract, which rises to a maximum as the hexane decreases, then falls as the linoxyn is formed in increasing amounts. As to be expected, the actual proportion of each of these components in a finished cement depends not only on the composition of the starting material but also on the conditions under which the reaction has been carried out. The effect of the temperature of oxidation is shown in Figure 7, where it is observed that an increase in temperature will produce a cement which has more hexane extract and less linoxyn. Since all of these cements gelled, it is obvious that the linoxyn, although present in smaller amounts, must have acquired a higher degree of polymerization which would, of course, be the case at a higher temperature. Incidentally this type of cement we would consider to be less desirable. The distribution of the oxygen extracts is shown in Table IV. For comparison, the values for the original mixture of linseed oil and rosin are also included. There is, of course, some oxidized material in the hexane extract, as is to be expected with mixed glycerides, but it is evident that

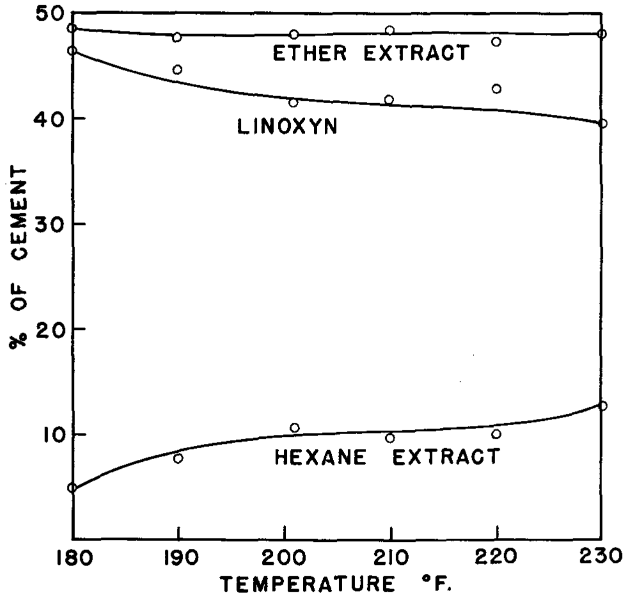

FIG. 7. Oxidation of linoleum binder—composition *vs.* oxidation temperature.

a great variety of oxygenated functional groups are formed. Ether oxygen is not included as we had no reliable way of determining it. Swern *et al.* have shown (3) that some functional groups interfere with the analysis of others. We followed the recommended procedure for analysis of these materials.

During the curing of linoleum at elevated temperatures the amounts of hexane and ether extracts decrease and the linoxyn content increases considerably, showing that oxidation as well as polymerization continues during the stoving process. This leads to the question of whether or not a linoleum cement when compounded and made into a sheet of goods will cure properly in the absence of oxygen. This is related directly to the degree of oxidation of the cement itself. If the cement is oxidized at a relatively low temperature, about 180°F., it will become well-oxidized and the goods will cure in a stream of pure nitrogen to a satisfactory point in about five times the normal length of time. If the cement is oxidized at a higher temperature, say about 220°F., it will gel sooner at a lower degree of oxidation and when made into a sheet it will show little sign of curing in a stream of nitrogen even after about 11 times the normal curing time. It will never cure to a satisfactory degree. The data are shown in Figure 8, where the effect of temperature of oxidation on curing time is clearly evident.

The solubility of linoleum cement is of interest in characterizing it as a thermosetting composition. We have already discussed the changes by which the cement during oxidation becomes progressively insoluble in nonpolar solvents; finally a substantial portion of it becomes insoluble even in polar solvents. This is evidence that a thermoset, cross-linked polymer has formed which cannot be dissolved again without the rupture of primary valence bonds. It cannot be considered to be a colloidal aggregate of molecules held together by molecular attraction or association of polar groups. This is shown by the fact that those treatments which result in the solution of linoxyn are only those which lead to hydrolysis or solvolysis through the breaking of bonds in ester groups. Since these would be important links in any cross-linked structure, whether formed by oxidation and/or polymerization, fission at these points alone would be enough to degrade the molecule to a predominantly linear form. Linoxyn will dissolve at room temperature in organic solvents which contain a small amount of sulfuric acid or phosphoric acid; it will dissolve at 100°C. in a solvent containing a little organic acid or a little water or alcohol. Once dissolved, the material will redissolve in any solvent for the ether extract but, if reheated and polymerized, it will again become insoluble.

THE CHEMISTRY involved in the production of floor coverings from polyvinyl chloride resins involves selection of a) the resins, based on molecular-weight range and distribution and copolymer composition, b) type and amount of plasticizers and stabilizers, and c) pigments and fillers. Considerable amounts of epoxidized soybean oil are used as stabilizer-plasticizers for polyvinyl chloride resins. No particular chemical change occurs in the resin during processing of the floor covering as long as stabilizers are present. It is to be noted, of course, that the preparation of the resin itself is not included in this discussion as it was in the description of the chemistry of linoleum cement. To date, the resins used are fairly conventional ones and are not as unique as the binder for linoleum.

The chemistry of the drying oils used in the felt base is similar to that of conventional varnishes and enamels. The traditional print paint-vehicles are composed of the usual types of bodied drying oils such as linseed, soybean, or tung oils, mixed with resins such as rosin-modified phenolics. The modern developments of styrenated or maleic-treated oils and alkyds have been used in present-day vehicles. It is necessary for the paints to be highly thixotropic so that they may be readily applied and quickly set, preventing the colors from running when the sheet is hoisted and hung vertically in a stove, as is done in some cases. This property of thixotropy is achieved by designing the paint so as to have a high degree of interaction between the liquids and solids. The important factors are the type and amount of surface of the pigments and extenders; the characteristics of the vehicle are less important.

Recently the production of printed felt-base has shown the effects of the increased popularity of the so-called roto-vinyl floor covering. In this product the felt is coated and sealed with synthetic resin coatings, then designs are applied by rotogravure cylinders or rolls, which use an ink in a vinyl resin vehicle. A vinyl resin wear coating is then put on. The ad-

TABLE IV

Functional Groups in Extracts Mols per 100-g. Extract

	Fatty acid	Rosin acid	Ester	Carbonyl	Hydroxyl	Oxirane	Peroxide	Total
Hexane	.055	.075	.25	.044	.039	.029	.003	.49
Ether	.030	.060	.43	.098	.095	.026	.011	.75
Original mixture		.035	.31				......	.345

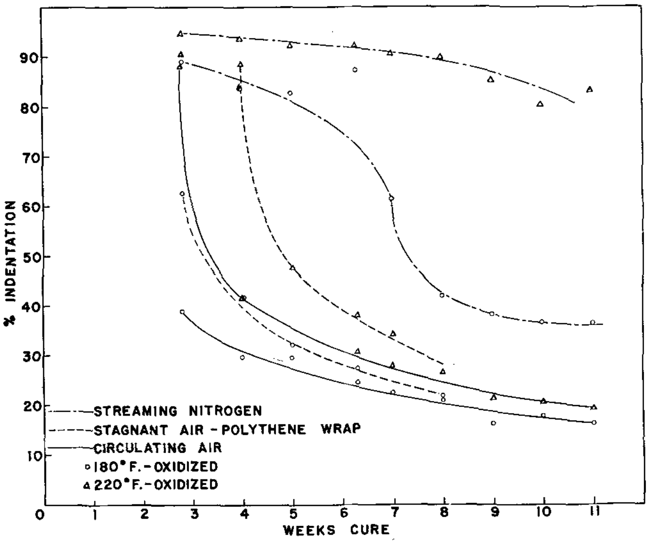

FIG. 8. Curing of linoleum binder in various atmospheres at 90°C.

vantages of this product are greater variety of design and better color. The wearing surface is about 3.5 to 5 mils thick, compared to 4 to 6 mils for printed felt-base. It is expected that this product will replace a substantial part of the drying-oil type.

A few general remarks may be made to compare the drying oil-based floor coverings with the synthetic resin ones. Linoleum could be improved in resistance to moisture, especially alkaline moisture as is present in concrete floors on grade, and in color, as the binder is inherently amber-colored. Polyvinyl chloride floor coverings could be improved in stability as the resin tends to degrade in light and air, in indentation resistance since it is thermoplastic, and in stain and soil resistance since the plasticizer tends to retain dirt. Polyvinyl chloride floor coverings are superior to linoleum in abrasion resistance although this is offset by the thinner wearing surface, in color and in water and in alkali resistance. They are limited by higher price, difficulty in retaining the original appearance, and by thermoplasticity.

If one wishes to increase the use of drying oils in floor coverings, it is obvious that improvements must be made in the drying-oil products. The comparisons just made can serve as a basis for a research program to use the chemistry of drying-oil systems to provide in the binder better water and alkali resistance, clear color, and rapid processing at low cost. With respect to costs the price of linseed oil, now about 14¢, is often compared with that of polyvinyl chloride at about 23¢. It would be more realistic, in my opinion, to compare linseed with vinyl chloride at 11¢, or ethylene at 5¢. Normally the conversion of monomeric drying oils to polymeric products is less expensive than the conversion of synthetic monomers so that some margin is available for new developments based on the application of polymer chemistry to drying oils. This is the only hope we see for increasing the use of drying oils in floor coverings.

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Degradation of Drying Oil Films

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The need for an understanding of the processes of degradation has led to continued research in various academic and industrial laboratories. And whether the justification for such work is an increase in human knowledge or a more marketable product, there have been basically two approaches, one empirical and one analytical. Both are valid, useful, and even necessary, and together they have produced a consistent picture of the chemical reactions which produce degradation and the physical manifestations of these reactions.

The physical manifestations of deterioration of a particular film, polymerized linseed oil, are many: loss of gloss, erosion, yellowing, embrittlement, loss of adhesion, cracking, to mention a few. All are not equally important in every application, but all are the inevitable consequences of the same sequence of chemical reactions. Moreover these are the same chemical reactions which polymerize the oil into a film; they are primarily oxidative. The site of the oxidation is the unsaturation in the molecule so that these behave as olefins rather than esters, and the chemistry of the oxidative degradation is similar in many respects to that of rubber and other unsaturated polymers.

The classic researches of Bolland and Gee (1, 2) and Farmer (3) have demonstrated that the absorption of oxygen by ethyl linoleate leads to the formation of hydroperoxides which decompose to yield various radical products, which may, in turn, induce low molecular weight vinyl polymerization. These steps are represented by the reaction schemes given in Tables I and II. The termination steps are the same in both cases, and whether 2R· radicals or 2ROO·

TABLE I
Mechanism for Hydroperoxide Formation

Initiation						
RH	+	O_2	⟶	R·	+	·OOH
Propagation						
R·	+	O_2	⟶	ROO·		
ROO·	+	RH	⟶	ROOH	+	R·
Termination						
R·	+	R·	⟶	RR		
ROO·	+	R·	⟶	ROOR		
ROO·	+	ROO·	⟶	ROOR	+	O_2

$R = CH_3(CH_2)_4CH{=}CH{-}\dot{C}H{-}CH{=}CH(CH_2)_7COOEt$

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