colloidal formations is strengthened by the fact that increase of viscosity does not occur until the refractive index and bromine value become constant, and that up to the point preceding gelation the molecular weight of the polymers does not exceed the dimeric form.

The above observations enable a partial visualization of the mechanism of drying oil polymerization.

(1) Polymerization is preceded by isomerization of the unsaturated acids containing two or three double bonds resulting in a conjugated system. This theory is supported by direct analytical methods and also by the fact that triolein, which is unable to form a conjugated system, cannot be polymerized.

(2) The conjugated systems build larger molecules until a semi-rigid structure is reached, resulting in gelation.

(3) Tung oil already containing a conjugated system is capable of almost instantaneous polymerization, while nonconjugated oils first must undergo isomerization, and hence the much slower progress of polymerization.

(4) When the required amount and proper size of molecules are built, colloidal forces cause gelation.

Pentaerythritol Drying Oils

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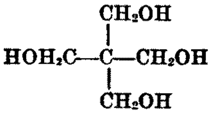
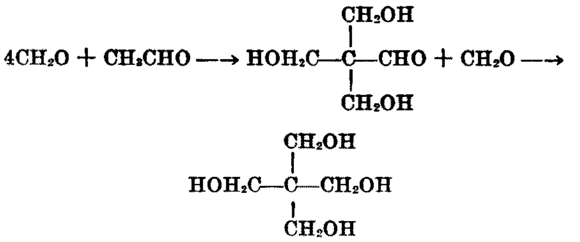
Pentaerythritol (tetramethylolmethane) the preparation of which was reported in 1891 by Tollens and Wigand (12) is a tetrahydric, primary alcohol having a quartenary carbon atom and the structure



$$HOH_2C-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2OH$$

The name pentaerythritol is an unfortunate misnomer since it is not accurately descriptive and is also difficult to pronounce; nevertheless, the usage is firmly established and it seems best to retain it.

Pentaerythritol does not occur in nature but is manufactured by the alkaline condensation of formaldehyde and acetaldehyde. The reaction occurs more or less stepwise with the preliminary aldol condensation to form pentaerythrose followed by a Cannizarro-type reduction to the alcohol:



$$4CH_2O + CH_3CHO \longrightarrow HOH_2C-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CHO + CH_2O \longrightarrow$$

$$HOH_2C-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2OH$$

Pure pentaerythritol melts at 261-264° C. (corrected), and occurs as a white crystalline solid resembling granulated sugar in appearance and taste. A technical grade which is about 85% to 90% pure is supplied to the paint and varnish trade, and this has a combining weight of approximately 35.7 instead of the theoretical 34.0.

Unsaturated fatty acid esters of pentaerythritol were prepared over fourteen years ago and were patented by Krzikalla and Wolf (10). Their French patent describes the preparation of the soy bean oil fatty acid ester and the German patent discloses the preparation of a varnish by esterifying a mixture of rosin and linseed oil acids. Bruson (4) mentioned preparing mixed fatty acid esters and states that they have "special drying properties." Gauerke (8) described a method of preparing a complex drying oil by alcoholizing tung oil (the natural glyceride) with polyhydric alcohols including pentaerythritol and then esterifying with linseed oil fatty acids. In 1936 Arvin (1) was granted a United States patent on the soy and linseed esters. Arvin's and Gauerke's processes recommend the use of litharge as an esterification catalyst, but our work has demonstrated that such practice is undesirable as will presently be shown. Arvin prepared paints, enamel, and varnish from his pentaerythritol drying oils and stated that in comparison with the corresponding glycerol esters the pentaerythritol esters were superior with regard to

1. Drying time
2. Gloss
3. Flexibility
4. Hardness
5. Toughness
6. Durability
7. Yellowing

This paper presents data which have been obtained from preparing drying oil acid esters of the technical grade of pentaerythritol, trademarked "Pentek." This product has an average hydroxyl content of 47.2% instead of the theoretical value of 50% for pure pentaerythritol. The reduced hydroxyl content is at least in part caused by the presence of about 15% dipentaerythritol. In addition to original data, because of the unfamiliarity of most American varnish chemists with the work done by the Russians, Drinberg and Blagonravova, edited translations of portions of a few of their articles are included where the data are pertinent.

Film Properties

The drying of the pentaerythritol ester of linseed acids is catalyzed in approximately the same manner as is linseed oil, both cobalt and manganese being powerful driers. However lead is poorly tolerated and ordinary lead naphthenate precipitates out; furthermore it is not as powerful a drier, *per se*, as calcium which is retained well and indeed lead is apparently an anti-drier. These statements are substantiated by Table I which records the tack free drying times (finger-tip method, films on glass) of boiled pentaerythritol-linseed acids ester containing the designated amounts of metal in the form of naphthenates. It may also be noted that the combination

TABLE I

Drying Catalysis

Drier	Drying Time, Hours
0.03% cobalt	7
0.03% manganese	9
0.01% cobalt + 0.01% manganese	6
0.30% calcium	35
0.30% lead	48
0.30% zinc	48
0.06% iron	36
none	40

cobalt plus manganese is more effective than either alone, as is to be expected; zinc is apparently inactive while iron shows some slight effect. In a set of outdoor durability tests on a variety of pentaerythritol-type esters (including those listed in Tables II and III), eleven oils containing 0.03% cobalt, 0.03% manganese, 0.3% calcium, and 0.3% lead had weather resistance inferior to controls with the lead omitted, four were not decisive, and two were improved with lead. This demonstrates that in general, lead is undesirable as a siccative. Inspection of the films as they dry indicates that neither lead nor calcium are necessary to promote through-dry since this seems to occur naturally.

In Table II several pentaerythritol esters of drying oil acids other than linseed are listed together with their drying times (using 0.03% cobalt, 0.03% manganese, and 0.5% calcium, to the tack-free stage by the finger tip method, films on glass) and outdoor durability (two coats of clear oil plus the same driers, on maple panels, exposed at Garfield, N. J., 45° to horizontal, facing south, the times recorded being those to failure to the point where the wood was no longer protected). The pentaerythritol ester of tung acids could not be made with an acid number below 30 without gelation although two Chinese investigators have reported it (13).

TABLE II

Drying Time and Durability of Pentaerythritol Esters

Oil Acids	Tack Free Drying Time	Durability, Months
Oiticica	5 hours	19
Dehydrated Castor [a]	5 hours	7
Fractionally distilled fish oil [b]	5 hours	12
Fractionally distilled soy oil [c]	7 days	3

a. Woburn Degreasing Co., "Isoline."
b. Armour & Co. "Neo Fat No. 19."
c. Armour & Co. "Neo Fat No. 23."

In Table III a comparison is given of pentaerythritol esters of linseed and soy acids with other polyhydric alcohol esters, all of which were bodied to 13 ± 0.2 poises before testing. The drying time data have the same significance as in Table II, while the per cent yellowness increase was determined by measuring the light transmission with the amber, blue, and green filters of a Hunter Reflectometer, and calculating the fraction $\frac{A-B}{G}$.

TABLE III

Polyhydric Alcohol Esters

	Tack Free Drying Time	% Yellowness Increase	
		Light	Dark
Linseed Acids Ester of:			
Pentaerythritol	15 hours	4.7	4.1
Erythritol	32 hours	......	......
Trimethylolpropane	15 days	......	......
Glycerol	7 days	......	......
Soy Acids Ester of:			
Pentaerythritol	18 days	5.3	2.9
Erythritol	21+ days	......	......
Natural Glycerides:			
Linseed Oil	7 days	33.4	16.8
Soy oil	30+ days	......	......
Tung oil	3 hours	......	......

Determinations were made immediately after drying and again after storage for one year in diffuse daylight and in the dark; the increase in one year is recorded.

It may be seen that the drying times of the pentaerythritol esters are considerably shorter than those of the other polyhydric alcohol esters, and that the linseed acids ester of pentaerythritol is much less subject to yellowing than the natural glyceride.

Drinberg (6) prepared the linseed acids ester of more or less pure pentaerythritol which he called "pentol." He investigated its properties and made detailed comparisons with tung oil, raw and bodied (3 hours at 290°C.) linseed oil, a bodied (1 hour at 290-300°C.) blend of two parts tung and one part linseed (which he termed "tung dicol"), a bodied "pentol dicol" consisting of two parts "pentol" and one part linseed, the glycerol ester of a fractionated fish oil (named "clupanodol"), and dehydrated castor oil. His results are compiled in Table IV.

From this table the following conclusions may be drawn:

1. The drying time of "pentol" approaches that of tung oil and the drying times on the bodied blends with linseed are apparently faster than the tung-linseed blend, although probably no attempt was made to body these blends to the same degree.
2. The hardness of the pentaerythritol ester films is notably greater than that of the linseed oil films, and even exceeds tung oil.
3. The lower benzene solubility of "pentol" probably indicates that a greater degree of cross-linking occurred during the drying than with the other oils.

TABLE IV

Drinberg's Drying Oils

Oil	d_{20}^{20}	n_{D20}	Acid No.	Iodine No.	M.W.	Drying Time		Hardness	Benzene Solubility, Pct.	Tensile Strength	Elasticity	Moisture Permeability	Swelling
						Dust Free	"Complete"						
Pentol	.9541	1.4914	3.5	155	1411	2.5	6.0	52.2	13.4	43.5	88.5	80	0.6-1.6
Pentol Dicol	....	....	6.4	153	....	1.25	3.0	70.0	29.1	......	88.5	67	0.0-0.5
Clupanodol	.9923	1.4110	17	203	1009	1.0	5.0	120.0	10.3	48.0	72.3	186	3.9
Dehyd. Castor	.9695	....	23.5	59	....	7-8	48.0	36.0	36.2	......	91.9	114	8.7
Raw Linseed	.9342	1.4831	2.6	186	861	10.0	24.0	25.5	49.0	24.3	84.7	148	2.5-3.4
Bodied Linseed	.9741	1.4930	4.0	119	1173	7.0	16.0	23.5	20.5	37.6	83.2	90	2.5
Tung	.9373	1.5190	8.9	160	802	0.5-1	3.0	43.6	27.2	30.5	......	107	3.3
Tung Dicol	....	1.4947	5.4	133	....	2.0	4.5	25.4	36.9	......	84.1	115	2.1-4.7

The Molecular Weight was determined cryoscopically, probably by the Rast method.
The Hardness was determined according to Walker and Steel (7) using films containing 0.12% Co dried on glass.
The Tensile Strength (Kg./cm.^{2}) was determined on free films about 50 microns thick.
The Elasticity measures per cent elastic deformation.
The Permeability is the milligrams of water penetrating through one cm.^{2} per micron of thickness per day in Gloor's (9) apparatus.
The Swelling was also determined according to Gloor (9) and is expressed in milligrams of water absorbed by 1 c.c. of film.

Notice that the functionality increase due to pentaerythritol has caused roughly the same degree of cross-linking as the increase brought about by the unsaturation in the high-clupanodonic fatty acid.

4. The tensile strength figures indicate that polymerization is further advanced in "pentol." Also stronger, tougher films are probably obtained.

5. Although the exact meaning of Drinberg's elasticity data is not too clear, he states "The numerical data obtained on the elasticity indicate that in spite of a very high degree of hardness, the pentol films have the highest elasticity."

6. The raw linseed and "clupanodol" films have the highest moisture permeability whereas the "pentol" and "pentol dicol" have the lowest, even lower than tung oil. The lowest swelling figures also indicate that "pentol" is highly water resistant.

Drinberg also offers the following observations regarding ageing of films, "Observations made during one year do not show any noticeable changes in the pentol, pentol dicol, and tung films. Enamel coatings of pentol do not change in two years when exposed to atmospheric conditions. The films changed but little during three years inside of buildings."

Blagonravova and Drinberg (3) prepared the pentaerythritol esters of unsaturated fatty acids with only one double bond such as pure oleic and erucic (C_{22}) acids, the glycerol esters of which did not dry. Pentaerythritol tetraoleate dried dust-free in 48 hours and "completely" in 60 hours; the erucate dried dust-free in 216 hours but did not dry hard.

Esterification Rates

A comparison of the rates of esterification of linseed fattyacids with pure pentaerythritol and with erythritol (the straight-chain, tetrahydric alcohol $CH_2OHCHOHCHOHCH_2OH$) is given in Figure 1.

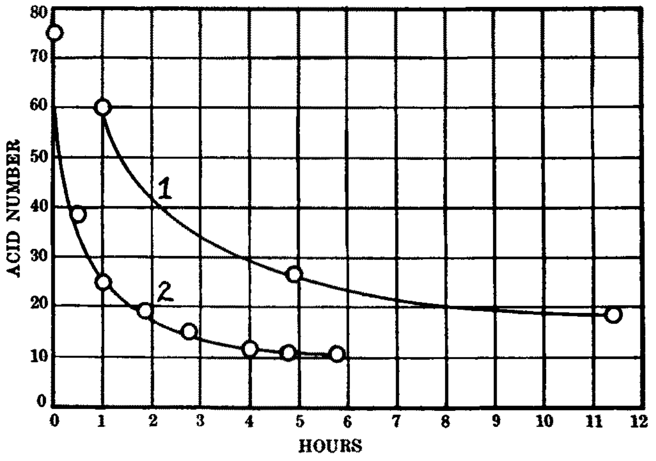


FIG. 1. Esterification of Linseed Oil Acids at 250°C. under CO_2.
1—Erythritol. 2—Pentaerythritol.

These data were determined by heating stoichiometric amounts of the acid and alcohols at 250°C.(482°F.) in an atmosphere of carbon dioxide using constant agitation. Samples were periodically removed, immediately cooled, and titrated with N/10 sodium hydroxide solution to determine the acid number, which values are plotted against time elapsed. A considerable difference in reaction rate exists between erythritol and pentaerythritol, the erythritol esterifying more slowly. This undoubtedly results from the secondary alcohol groups of erythritol.

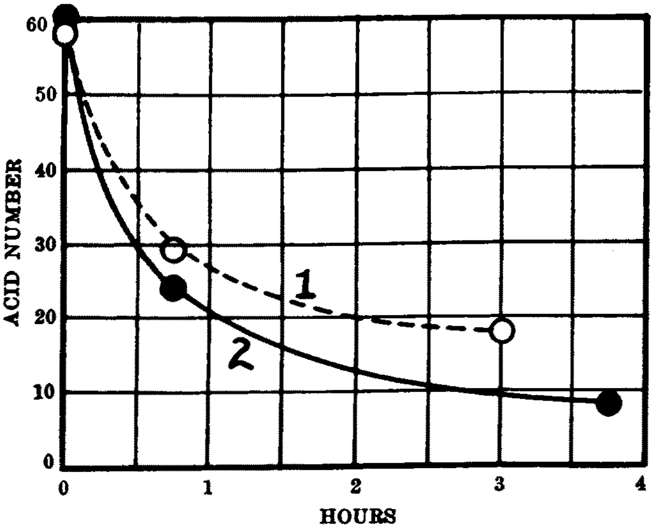


FIG. 2. Pentaerythritol Esterification of Soy Oil Acids.
1—Under Carbon Dioxide. 2—With Hydrocarbon Azeotrope.

Figure 2 shows the effect of carrying out the esterification in the presence of a hydrocarbon azeotrope. By esterifying soy acids with the stoichiometric amount of pentaerythritol using a mixture of the isomers of triisopropyl benzene (boiling range 236-237.5°C., 457-459°F.) to remove the water of esterification, the time required to reach an acid number of 10 is reduced to one-third of that required for simple heating under carbon dioxide. The rates of esterification of linseed acids by this method, using several alcohols, are given in Figures 3 and 4. At 200°C. (392°F.) the rates are somewhat too slow for commercial production. The effect of adding calcium naphthenate as an esterification catalyst in addition to the azeotropic solvent is also shown in Figure 3 and it may be seen that the rate is considerably increased. At 230°C. (446°F.) the rates are of practical velocity.

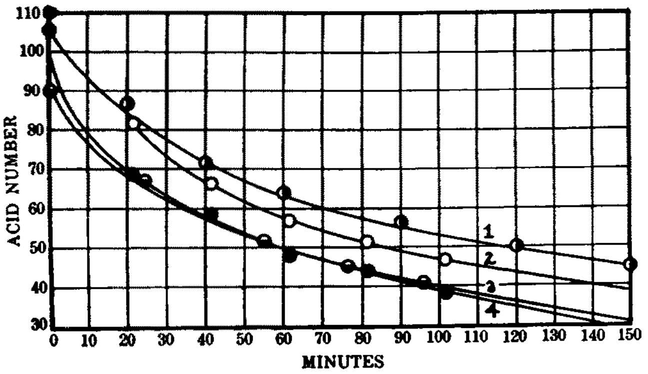


FIG. 3. Esterification of Linseed Oil Acids at 200°C.
1—Glycerol. 2—Pentaerythritol. 3—Trimethylolpropane.
4—Pentaerythritol plus Calcium Naphthenate.

The effect of using an excess of technical pentaerythritol (hydroxyl value: 47.2%) on the esterification rate of linseed acids is shown in Figure 5. These reactions were carried out with constant stirring at 220°C. (428°F.) under an atmosphere of carbon dioxide (without azeotrope or catalyst). The initial drop in acid number is greater with ten per cent excess pentaerythritol, but after three hours the difference between five and ten per cent excess is negligible; therefore it is unnecessary to use more

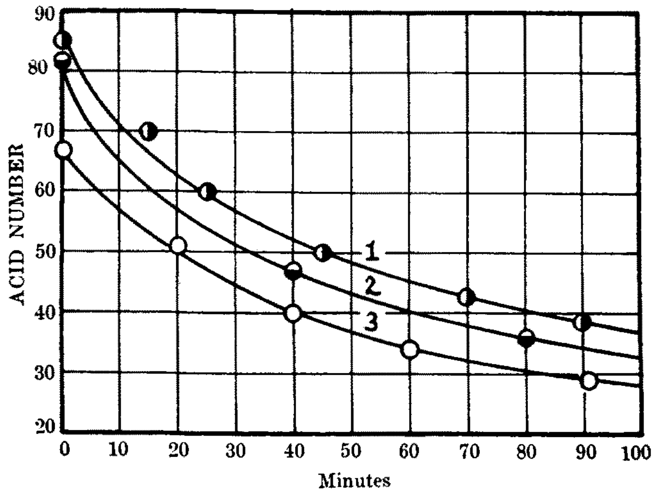


FIG. 4. Esterification of Linseed Oil Acids at 230°C.
1—Glycerol. 2—Trimethylolpropane. 3—Pentaerythritol.

than five per cent excess and the advantage gained by this amount is not great.

Blagonravova and Drinberg (3) investigated several procedures in attempts to make the esterifications go at reasonable speeds. They concluded that passing gaseous HCl through the reaction mixture was highly undesirable as was also the use of anhydrous zinc chloride and calcium chloride because the acid numbers obtained were always high, the oils were too highly bodied, and the oils might contain chlorine. The use of sulfuric acid as an esterification catalyst was unsatisfactory because of charring and gelation. They finally concluded that the best procedure was simply to heat from 25 to 50% excess of pentaerythritol with the fatty acid at 200-220°C. for 6 to 10 hours. As mentioned later, these conditions are not to be recommended in commercial practice.

Alcoholysis

What may be considered to be of a special type of esterification is involved in the alcoholysis of natural glycerides with pentaerythritol. This is a convenient and economical method of preparing partial or hydroxy esters of mixtures of glycerol and pentaerythritol which are suitable for further reaction with

a. drying oil acids to form improved drying oils
b. resin acids to form varnishes, and
c. polybasic acids to form alkyd resins.

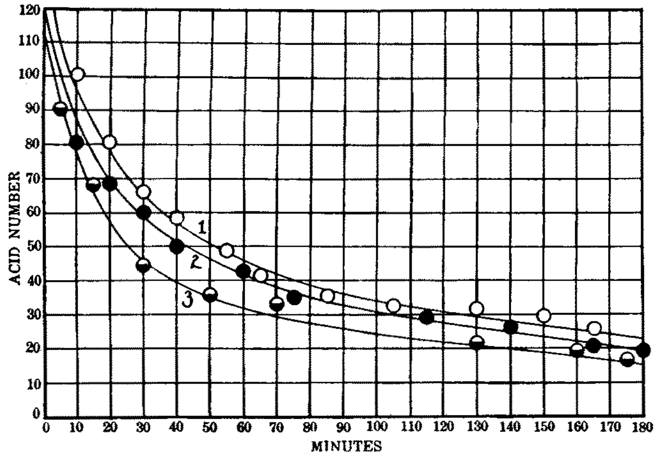


FIG. 5. Esterification of Linseed Oil Acids.
1—Stoichiometric, Pentaerythritol. 2—5% Excess Pentaerythritol. 3—10% Excess Pentaerythritol.

This procedure is similar to the "monoglyceride" process as applied (using glycerol) to the production of alkyd resins. Both Gauerke (8) and Robinson (11) mention the use of pentaerythritol as an alternative alcohol in preparing alkyds by this method.

Pentaerythritol will alcoholize soy oil, for example, if heated with agitation at 280°C. (536°F.) for about one hour; this necessitates a rather high temperature and frequently results in undue bodying and color formation and is generally undesirable. The time required may be greatly shortened and the temperature reduced by using catalysts such as the oil-soluble salts of lithium, calcium, strontium, barium, zinc, and cadmium (5).

Calcium naphthenate is particularly effective and will promote the alcoholysis of alkali refined linseed oil with 5 per cent of its weight of pentaerythritol in fifteen minutes at 250°C. (482°F.) in concentrations as low as 0.005% expressed as metallic calcium and based on the weight of oil. Naphthenates of lead and cerium are also active, and litharge has been suggested (8), but such materials invariably cause dark colors to be formed, and tend to precipitate out later. As a general rule, it may be stated that in the reactions of the pentaerythritol-type alcohols, the presence of lead is nearly always deleterious.

TABLE V
Alcoholysis Catalytic Activity

Metal Salt	Minutes Required for Alcoholysis
Aluminum	....
Barium	14
Bismuth	....
Cadmium	20
Calcium	5
Cerium	19
Cobalt	....
Chromium	....
Copper	....
Iron	....
Lead	1
Lithium	1
Magnesium	....
Manganese	....
Mercury	....
Nickle	....
Strontium	48
Thorium	....
Zinc	31

Table V lists alphabetically the metals which, as naphthenates, stearates, or abietates, were tried for alcoholysis catalytic activity. The procedure for testing consisted of adding 1.0% of the salt to soy bean oil, heating to 230°C. (446°F.) and then adding 24% technical pentaerythritol and holding at 230°C. (446°F.) until the pentaerythritol had dissolved (the time required being noted in the table), or for at least one hour if it did not dissolve. In Table V, where no times are given, the pentaerythritol had not dissolved within one hour and these metals were classed as having no significant activity. The simple end point of observing whether the alcohol has dissolved checks well with subsequent testing the solubility in ethanol or methanol.

Table VI shows the relative ease of alcoholysing soy oil at 230°C. with pentaerythritol as compared with other alcohols, using 1.0% calcium naphthenate. It may be noted that primary alcohols respond readily to the catalytic action of calcium naphthenate but that secondary alcohols (including glycerol) respond slowly or not at all.

TABLE VI

Promotion of Alcoholysis by Calcium Naphthenate

Alcohol Used	Time Required
Pentaerythritol	5 minutes
Glycerol	60 minutes
Trimethylolpropane	0.5 minute
Ethylene glycol	1 minute
Tetraethylene glycol	2 minutes
Sucrose	Not in 4 hours
Mannitol	Not in 4 hours
Polyvinyl alcohol	Not in 4 hours

The use of any catalyst may be avoided if the drying oil is heat treated or bodied lightly before adding the pentaerythritol (14). A comparison of the use of 1% calcium naphthenate catalyst in combination with alkali-refined linseed oil as contrasted with elimination of the catalyst by using a vacuum bodied linseed oil having a viscosity of 15 poises is given in Figure 6 where the per cent of theoretical hydroxyl value as calculated from acetyl number determinations is plotted against time of heating at 250°C. (482°F.). It is apparent that the maximum hydroxyl value is obtained after about thirty minutes, but it is practical to heat for only ten minutes. It should be noted that the available hydroxyl content is slightly greater when the bodied oil was used.

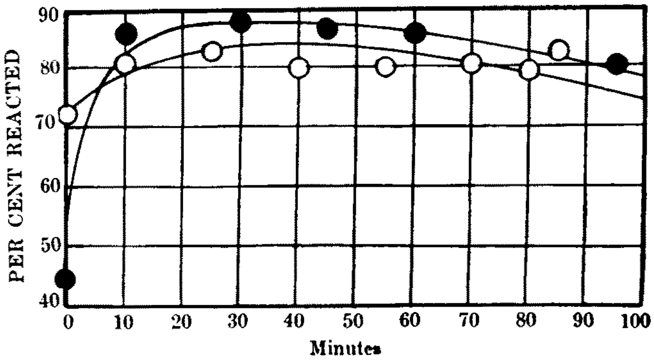


FIG. 6. Alcoholysis of Linseed Oil With Pentaerythritol. Upper Curve—Bodied Oil. Lower Curve—Calcium Catalyst.

Blagonravova *et al.* (2) have compared the alcoholysis of refined linseed oil with glycerol and pentaerythritol in some detail, and part of their results are quoted here:

"For practical purposes (for example in the preparation of alkyd resins) it is satisfactory to carry out the exchange esterification with 25-30% of glycerol during 50-55 minutes, at a temperature of 240°C., and in the presence of 0.04-0.06% CaO. The mixture of various glycerides obtained reacts easily with dibasic acids (phthalic, maleic).

"The first preliminary experiments showed that in the exchange esterification with pentaerythritol, the latter should not be present in great excess, since the unreacted pentaerythritol carbonizes and forms a dense precipitate on the bottom of the reaction apparatus. Although the alcoholization with glyceride yields best results at a ratio of 3-5 mols of glycerol per mol of oil, the exchange esterification with pentaerythritol necessitates a maximum ratio of 2 mols pentaerythritol per mol of oil. The following shows the result of alcoholizing one mol of refined linseed oil with varying amounts of pentaerythritol at 220°C. in the presence of 0.04-0.08% CaO. The per cent column is based on the oil.

Pentaerythritol (94.2% pure)		Acetyl Number
Mols	Per Cent	
2.0	31.0	134.7
1.6	25.0	121.6
1.35	20.75	107.3
1.05	16.25	68.6
0.75	10.4	65.2

"In another set of experiments, 20.75% pentaerythritol was reacted for 3 hours at the temperature noted below in the presence of 0.04-0.08% CaO.

Temperature, °C.	Acetyl Number
270	20.8
260	61.8
250	80.7
240	107.3
230	128.5
220	132.6

"From the data presented in the above tables it is evident that (1) the degree of alcoholysis increases with the increase of pentaerythritol and (2) an increase of the temperature with the same amount of pentaerythritol lowers the amount of free hydroxyl. This may be explained evidently in the same manner as is the case with the reaction with glycerol, i.e. by the formation of compounds of the type of ethers.

"As mentioned above, calcium oxide in the amount of 0.04-0.08% of the weight of the oil was used for catalyst in the above experiments. However, the reaction with this catalyst proceeds very slowly, being completed only after 6 hours in the case of small laboratory charges. An increase in the amount of the catalyst does not result in an acceleration of the reaction. Experiments with sodium hydroxide which is a more active catalyst were instituted for this purpose.

"However, when introducing caustic directly into the reaction mixture, a partial saponification of the oil takes place. Satisfactory results are obtained in cases when the caustic is preliminarily fused with the pentaerythritol by a careful heating of the mixture till a brownish fluid mass is obtained which solidifies on cooling. The process of alcoholization in the presence of sodium hydroxide takes place at 205-210°C., requiring 2.5 hours; thus the use of caustic as a catalyst accelerated the process considerably.

"In the alcoholization of oils with pentaerythritol, a considerably more complicated process takes place than in the alcoholization with glycerol. Here various mixtures of incomplete glycerol and pentaerythritol esters may be obtained.

"The product of exchange esterification of oil with pentaerythritol is insoluble in ethyl alcohol, while the mono-ester of pentaerythritol and linseed oil acids obtained by direct esterification is easily soluble in alcohol. Thus we may assume that compounds of the type of di- and possibly tri-substituted esters are formed in the alcoholization."

In view of the original data reported immediately preceding this quotation it is evident that the soluble salts of the metals mentioned are far more efficacious than the commonly used (with glycerol) sodium hydroxide or calcium oxide.

Blagonravova *et al.* explain the low acetyl numbers obtained in some circumstances by postulating the formation of ethers. If this is so, it probably results solely from etherification of glycerol because it has not been possible to prepare pentaerythritol ethers by simple heating.

The Russians also note that the products of their alcoholization were insoluble in ethanol. When linseed oil is pentaerythritolized by using calcium naphthenate, as described above, the cooled oil contains a white precipitate which might be suspected of being pentaerythritol; this is not so however because the entire product, precipitate and supernatant oil, is soluble in 4 or 5 volumes of methanol or ethanol, whereas pentaerythritol is not very soluble in the alcohols. Actually it is not necessary to use this solubility test to detect completion of alcoholysis, because it has been found that attainment of solubility coincides with disappearance of pentaerythritol from the hot reaction mixture. It is thought that the discrepancies of low hydroxyl value and poor alcohol solubility in the Russian paper are caused by the severe conditions they found necessary which resulted in probably nearly complete liberation of glycerol and its subsequent loss or destruction. It should be noted that a rather small percentage of pentaerythritol will theoretically release *all* of the glycerol, as is indicated in the following table.

TABLE VII

Theoretical Mixtures Obtained by Pentaerythritolysis

Per Cent Pentaerythritol	Theoretically Possible Ester Mixture
3.86	Glycerol diester and pentaerythritol tetraester
7.72	Glycerol mono ester and pentaerythritol tetraester
11.58	Free glycerol and pentaerythritol tetraester or glycerol mono ester and pentaerythritol triester
15.45	Glycerol mono ester and pentaerythritol diester
19.31	Glycerol mono ester and pentaerythritol mono ester

Summary of Preparation of Pentaerythritol Drying Oil Esters

As the result of several years work which has involved numerous laboratory experiments, pilot plant production and customer service, the following remarks are offered as practical advice which should be helpful to those engaged in or contemplating the manufacture of the drying oil acid esters of pentaerythritol.

The pentaerythritol drying oils are rather simply prepared by heating together a mixture of the fatty acids and the polyhydric alcohol. It is usually desirable to charge all ingredients at room temperature into a closed kettle fitted with a powerful agitator and to heat the mass to reaction temperature while stirring.

Esterification seldom starts below a temperature of approximately 200°C. (392°F.). In the range of 200-230°C. (392-446°F.) which is a convenient reaction temperature, the alcohols usually melt, and because of their high specific gravity form a lower, immiscible layer which is subject to overheating. This is undesirable since pentaerythritol tends to decompose at temperatures somewhat above the melting point, forming undesirable by-products and a certain amount of carbon and other deleterious materials.

To hasten the speed of esterification as well as to discourage such decomposition and side reactions, it is important that the esterification reaction be carried out in a vessel which is equipped with suitable agitation equipment. This agitator may be of the turbine or propeller type and in any event should be so designed that it causes a flow of the reactants from the bottom of the reacting vessel toward the top or surface of the reaction mixture in such a way that it constantly lifts off of the bottom the heavier layers of melted alcohol. Paddle type agitators are usually not satisfactory. As soon as the pentaerythritol is partially reacted (presumably when only one hydroxyl group has been esterified) the partial ester so formed is then miscible in the hot reaction mixture and danger of discoloration or side reaction is thereby greatly lessened. Therefore, after the alcohol has dissolved, agitation need not be so violent as before; naturally, precaution should be taken not to whip air through oxygen-sensitive reaction mixtures.

In general, stoichiometric proportions of acids and the polyhydric alcohols may be used, although 2 or 3 per cent excess alcohol may aid in lowering the acid number without causing any deleterious action.

A blanket of carbon dioxide, nitrogen, illuminating gas, or other oxygen-free atmosphere may be maintained over the reaction mixture to aid in the maintenance of light colors. This is frequently done when unsaturated fatty acids are used, to prevent undue bodying.

Catalysts for promoting the esterification must be selected with caution. The use of strong acids such as sulphuric or paratoluene sulfonic is not recommended since these usually lead to the formation of dark colored products. Litharge has also been suggested (1) to promote this type of esterification, but it is not to be recommended because it definitely increases color formation and causes after-precipitation and in addition has no desirable siccative action on pentaerythritol esters for use in air-dried coatings. Substances which have been found to be excellent catalysts, and which will not darken the reaction mixture, include calcium naphthenate, calcium stearate, or limed rosin.

Other methods of increasing reaction speed depend on expediting the removal of the water of esterification. Naturally this may be aided by carrying out the reaction under a partial vacuum. An alternative to this is to add a water-immiscible, azeotropic solvent to the reaction mixture and to carry out the reaction in equipment designed to condense the evolved vapors and to return the water-immiscible solvent to the reaction mixture and at the same time to trap and run off the water formed. High boiling petroleum hydrocarbon solvents have been found to be particularly applicable to such use and at the same time they serve to exclude oxygen by replacing the air in the reaction vessel with solvent vapors.

In reacting pentaerythritol-type alcohols, it should be remembered that the esters may crosslink more easily than the corresponding glycerol esters, and therefore convert more easily to gels. Pentaerythritol esters of highly unsaturated fatty acids are sometimes excessively polyfunctional, and should be prepared with due precautions to guard against gelation.

Conclusion

The use of pentaerythritol in the drying oil field has been very successful. It seems to be the consensus of opinion among the users that "the stuff is here to stay." By using pentaerythritol instead of glycerol one may expect to obtain faster drying, quicker bodying, higher gloss, greater water resistance, better ageing characteristics, and harder and tougher films.

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