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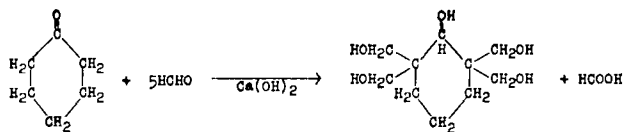
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Drying Oils From 2,2,6,6-Tetramethylcyclohexanol and Linseed Fatty Acids^{1,2}

HAROLD WITTCOFF, General Mills inc., Minneapolis, Minn.

THE value of employing polyhydric alcohols with a functionality higher than that of glycerol for the preparation of reconstituted drying oils has been demonstrated by several investigators. Thus Burrell (2, 3) has described drying oil fatty acid esters of pentaerythritol and the polypentaerythritols, whereas Brandner and co-workers (1) have described similar esters of sorbitol. This paper describes a) a study of the esterification of 2,2,6,6-tetramethylcyclohexanol (TMC) with linseed fatty acids, and b) the properties of the reconstituted oils.

TMC is a pentahydric alcohol with four hydroxyl groups which are primary and one which is secondary. It was first described in 1923 by Mannich and Brose (6), who prepared it by the condensation of the cyclic ketone, cyclohexanone, with formaldehyde in the presence of lime.



The pure material which melts at 131°C. is a white, beautifully crystalline solid with a hydroxyl content of 38.6%. The product used in the following investigations was prepared in the laboratory. It was technical in nature, possessing a hydroxyl content of 36.0 ± 0.5%. The pentaerythritol employed for comparative purposes was a commercial product known as "Pentek," which has a hydroxyl content of 47.0 ± 0.5% as compared to the theoretical value of 50.0%. The glycerol used was a redistilled U.S.P. reagent with a theoretical hydroxyl content of 55.3%. The linseed acids used were a commercial grade of distilled fatty acids.

The metallic stearates employed as esterification catalysts were prepared by the following procedure: a hot solution of pure stearic acid (6 g.) in alcohol (75 cc., 95%) was neutralized to phenolphthalein with alcoholic sodium hydroxide (0.2 N). The solution was diluted with hot water to a volume of 450 cc., and this was added with vigorous stirring to a 10% excess of the requisite metallic acetate in water (90 cc.). The precipitate was allowed to stand for one hour and then was filtered by gravity and

washed with water (500 cc.). The paper containing the precipitate was then placed on a Büchner funnel, suction was applied, and the product was washed with small quantities of alcohol and ether. The soaps were finally dried *in vacuo* at 70°C.

Esterification of TMC

All reactions were carried out azeotropically in a one-liter, three-necked, round bottom flask, equipped with standard taper joints and modified to include a thermometer well. The flask was heated by a "Glas-Col" heating mantle. One neck of the flask was equipped with a stirrer whereas a second neck contained a water trap of the Dean and Stark (4) type, in which was inserted a Claisen-type tube. In one neck of the Claisen head was placed a condenser and in the other a small dropping funnel. The third neck contained a standard taper joint, into which was sealed a U-shaped tube with an outside diameter of about one-fourth inch. One end of the tube reached below the surface of the reaction mixture and the other contained a stopcock. This tube provided a convenient means of sampling, for the application of a positive pressure of nitrogen in a balloon at the condenser outlet forced a sample of the reaction mixture out of the open stopcock of the U-tube.

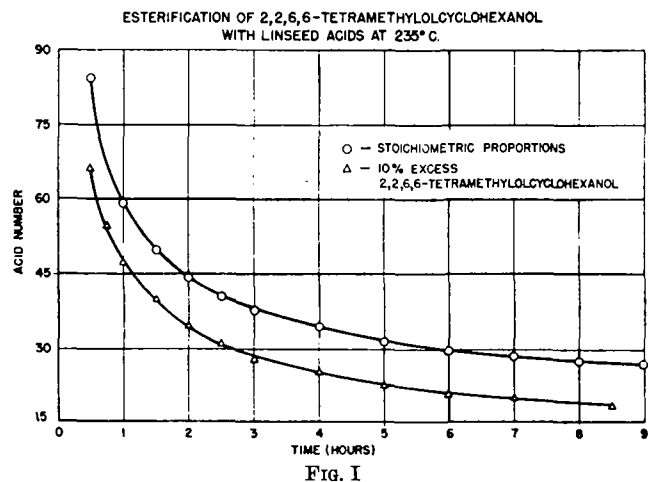
A xylene azeotrope was found to facilitate the esterification, the water of reaction separating in the Dean and Stark trap, whereas the xylene flowed back into the reaction vessel. The temperature depended upon three factors: the temperature of the "Glas-Col" heating mantle, the rate of stirring, and the amount of xylene in the reaction mixture. By keeping the first two factors constant, the temperature of the reaction was relatively easily controlled by the third means. The regulation of temperature by control of the amount of solvent has been described in some detail by Earhart and Rabin (5). Xylene could be added to the reaction mixture through the above-mentioned dropping funnel, whereas it could be removed through the water trap. By this means it was possible, with some degree of experience, to maintain a temperature constant within ± 1°. The xylene had an added advantage in that it provided an inert atmosphere for the reaction. Ordinarily 50 cc. of xylene was used at the start, a portion of which was allowed to fill the trap. The amount of xylene was adjusted by the above-indicated method as the reaction progressed.

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² Presented at 22nd annual fall meeting, American Oil Chemists' Society, New York City, Nov. 15-17, 1948.

The samples which were taken at intervals were desolvated, weighed, dissolved in a mixture of xylene and isopropyl alcohol, and titrated with 0.1 N sodium hydroxide to a phenolphthalein end-point. The starting time of the reaction was designated as that time at which the temperature reached 170°C. since it was here that homogeneity seemed to be achieved. Thereafter, the operating temperature was reached in 30 to 60 minutes, and once reached it was maintained constant by the above-outlined procedure.

The Uncatalyzed Esterification: The results of the uncatalyzed esterification studies are indicated in Figures I-III. Figure I shows the effect of stoichi-

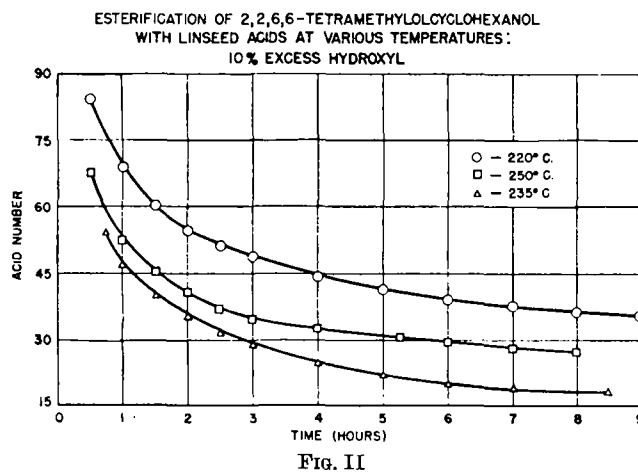


ometry on the uncatalyzed esterification at 235°C. When stoichiometric proportions of the alcohol and the acid were used, the rate of esterification was considerably slower than when 10% excess of alcohol was employed. The results of the two esterifications follow:

	Time (hr.)	Acid No.	OH No.	Color (Gardner)	Visc. at 25°C. (Gardner-Holdt)
Stoichiometric proportions.....	9.0	26.8	6.2	12	E-F
10% excess TMC.....	8.5	18.3	22.3	10-11	E-F

It will be seen in the first case that the acid number was in excess of the hydroxyl number by 20.6 even though they were equivalent at the start of the reaction. This may be shown to be equivalent to 12% excess acid. Accordingly, in the second case where a 10% excess of TMC was employed, the acid and hydroxyl numbers were practically equivalent at the end of the reaction. It is logical to assume, therefore, that in the uncatalyzed esterification a side reaction such as etherification has taken place to a small extent. Inspection of the data indicates that 90% of the reaction has taken place in the first hour. For this reason kinetic interpretation is precluded since the bulk of the data is concerned with the last 10% of the reaction; and in this region deviation would be expected from the second order kinetics which ordinarily characterize esterifications.

Figure II demonstrates the effect of temperature on the esterification. In each case a 10% excess of alcohol was used. It is immediately obvious from the curves that the uncatalyzed esterification proceeds more rapidly at 235°C. than it does at either the

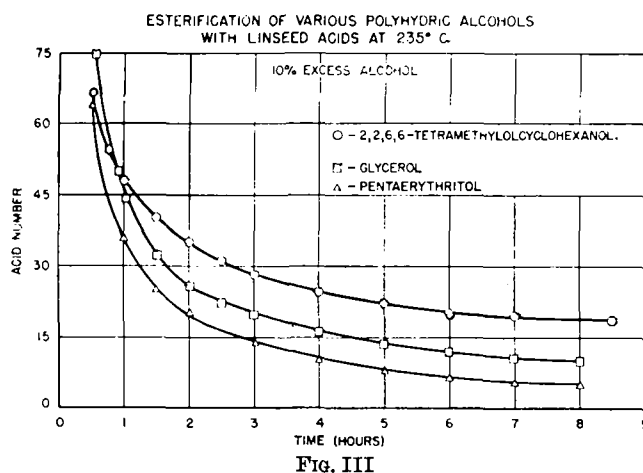


lower or the higher temperature. The reason for this becomes apparent from the following data:

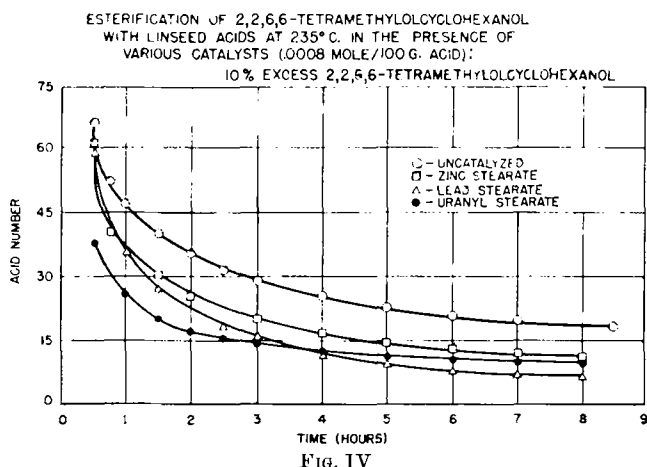
Temperature (°C.)	Time (hr.)	Acid No.	OH No.	Color (Gardner)	Visc. at 25°C. (Gardner-Holdt)
235	8.5	18.3	22.3	10-11	E-F
220	11.0	33.4	2.7	12-13	D-E
250	8.0	27.2	0	12	H

These data show that an equivalence of acid and alcohol was maintained only at 235°C. At 220°C. the hydroxyl groups were used up, probably because of side reactions such as etherification due to the longer heating period which was employed in an attempt to obtain a lower acid value. Thus the acid number at the end of the reaction was high. At 250°C. the side reactions apparently proceeded more rapidly than the esterification reaction so that all of the alcohol was consumed at the end of eight hours, and the acid content was still high. At 235°C., however, when 10% excess alcohol was employed initially, it was possible to maintain a balance between the two competing reactions of etherification and esterification such that equivalent quantities of the reacting groups were present at all times. In other words, at 235°C. the uncatalyzed esterification is rapid enough and the side reactions are slow enough to produce results of a practical nature. The effect of temperature on viscosity is well-illustrated by these experiments.

In Figure III the rate of esterification of TMC with linseed acids at 235°C. is compared with that of pentaerythritol and glycerol. In each case a 10%



excess of alcohol was used. The results are those which would be expected from the structure of the alcohols. The esterifications start out at about the same rate since, initially, unhindered primary hydroxyl groups are involved. Pentaerythritol is esterified most rapidly because it contains only primary hydroxyl groups. On the other hand, TMC is esterified most slowly because in addition to four primary

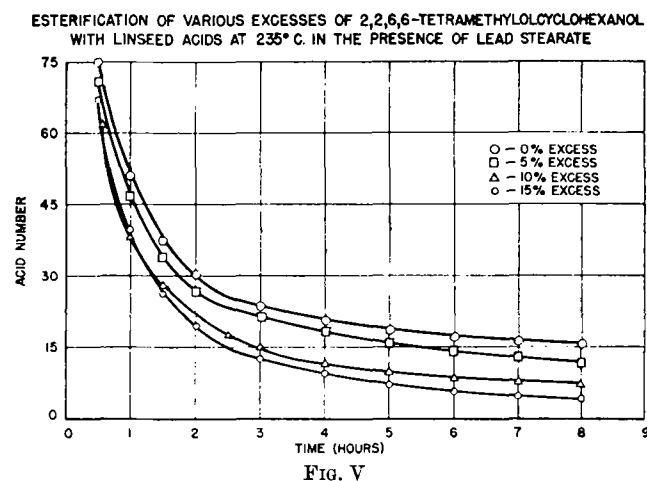


unhindered hydroxyl groups it contains a hindered secondary hydroxyl. As may be shown by models, this secondary hydroxyl group is undoubtedly more hindered than the secondary hydroxyl group of glycerol whose esterification rate is intermediate between that of pentaerythritol and TMC. The slower rate of esterification of the latter compound may be compensated for, as will be indicated later, by the use of appropriate catalysts. The properties of the three oils which were obtained in this series of experiments follow:

Alcohol	Time (hr.)	Acid No.	OH No.	Color (Gardner)	Visc. at 25°C. (Gardner-Holdt)
TMC.....	8.5	18.3	22.3	10-11	E-F
Glycerol.....	8.0	10.3	18.4	11	B-C
Pentaerythritol.....	8.0	5.4	11.3	11-12	C-D

The TMC oil possessed the greatest viscosity, a fact which is considered advantageous in many instances.

The Catalyzed Esterification: Figure IV demonstrates the catalytic effect of uranyl, zinc, and lead



stearates on the esterification of TMC when 10% excess alcohol is used. These were chosen as the most efficacious from a long series of stearates investigated. Their preparation has been described in the introduction. An arbitrary concentration of 0.0008 mole of catalyst per 100 g. of acid was chosen. Other effective catalysts included the stearates of tin, nickel, calcium, silver, aluminum, chromium, manganese, platinum, and iron.

Of the three catalysts, lead was the most effective, an acid number of seven resulting after eight hours of reaction. The properties of the reconstituted oils follow:

Catalyst	Time (hr.)	Acid No.	OH No.	Color (Gardner)	Visc. at 25°C. (Gardner-Holdt)
None.....	8.5	18.3	22.3	10-11	E-F
Uranyl stearate.....	8.0	10.9	7.7	15-16	G-H
Zinc stearate.....	8.0	11.0	4.3	12	E-F
Lead stearate.....	8.0	7.7	7.1	12	F-G

Only uranyl stearate affected the color markedly whereas uranyl and lead stearates caused the viscosity of the product to increase.

The catalysts precipitated when the reconstituted oils were cooled and thus could be removed by filtration.

Figure V demonstrates the effect of varying excesses of TMC on the esterification in the presence of lead stearate. From the graphs and from the following data it becomes apparent that an excess of 5-10% is practical and that there is no particular virtue in a larger excess.

Per cent excess	Catalyst	Time (hr.)	Acid No.	OH No.	Color (Gardner)	Visc. at 25°C. (Gardner-Holdt)
0	Lead stearate	8.0	15.6	5.9	11	D-E
5	Lead stearate	8.0	12.2	2.9	12	E-F
10	Lead stearate	8.0	7.7	7.1	12	E-F
15	Lead stearate	8.0	4.7	2.6	12	E-F

Figures VI, VII, and VIII compare the effect of these catalysts on the esterification of glycerol and TMC with linseed acids. It will be noted that the esterifications proceeded more rapidly at the start in the case of TMC due probably to the fact that it possesses twice as many primary hydroxyl groups.

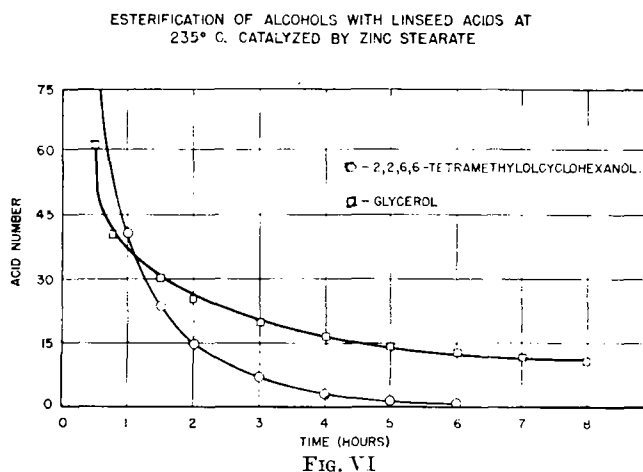


TABLE I
Drying Times for the Linseed Acid Ester of TMC
Under the Influence of Metallic Driers

Driers	Time (hours)				Remarks
	Initial Set	Set to Touch	Lint-free	Dried Hard	
None.....	40.0	46.0	49.0	51.0	Wrinkled film
.04% cobalt.....	1.8	2.3	3.0	9.0	Wrinkled film
.08% cobalt.....	1.2	2.0	2.6	7.0	Wrinkled film
.04% manganese.....	7.0	8.0	10.0	13.0	Wrinkled film
.08% manganese.....	6.5	7.5	8.0	12.0	
.25% lead.....	11.0	17.0	24.0	26.0	
.25% zinc ¹	26.0	33.0	40.0	45.0	
.25% calcium.....	17.0	24.0	27.0	29.0	
.25% aluminum ²	< 15.0	26.0	< 30.0	< 38.0	
.03% cobalt + .03% manganese.....	1.5	4.0	4.5	7.5	Wrinkled film
.03% cobalt + .25% lead.....	.75	1.5	2.3	6.0	
.03% cobalt + .25% calcium.....	.83	1.6	3.0	7.0	
.03% cobalt + .20% zinc.....	1.0	3.0	3.5	7.0	
.03% manganese + .25% lead.....	1.8	3.5	4.3	7.0	Wrinkled film
.03% manganese + .25% calcium.....	2.3	5.5	6.0	8.0	Wrinkled film
.03% manganese + .20% zinc.....	4.0	7.5	9.0	10.0	
.03% cobalt + .03% manganese + .25% lead.....	1.5	3.0	4.5	6.0	Wrinkled film
.03% cobalt + .03% manganese + .20% zinc.....	1.5	5.5	6.0	8.0	Wrinkled film
.03% cobalt + .03% manganese + .25% calcium.....	1.2	4.2	4.8	7.0	Wrinkled film

¹ Zinc drier was not compatible at this concentration and a precipitate resulted on standing. The supernatant material was used for the drying test.

² Originally a gel formed which disappeared after 24 hours.

ESTERIFICATION OF ALCOHOLS WITH LINSEED ACIDS AT
235° C. CATALYZED BY LEAD STEARATE

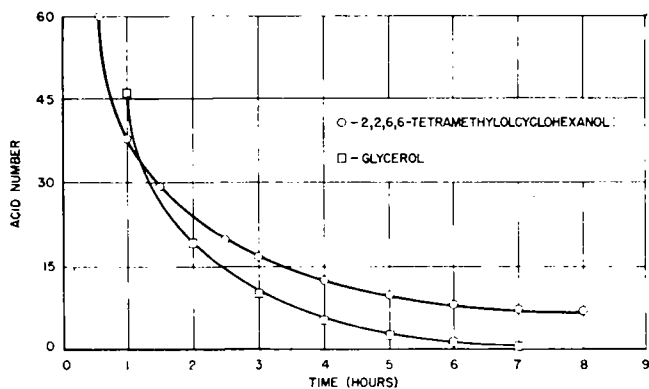


FIG. VII

The Optimum Procedure for the Esterification of TMC: TMC is best esterified azeotropically in an apparatus of the type previously described. Certain obvious advantages accompany the azeotropic procedure such as decreased reaction time, lighter color of the final product, more uniform heating which assures a homogeneous product, and complete removal of the water which allows an accurate estimation of the extent of reaction. Non-azeotropic esterification is also feasible, however, and is best accomplished in the presence of an inert gas such as carbon dioxide or nitrogen. As already indicated, for optimum results a 5-10% excess of TMC should be used together with lead stearate as a catalyst in the concentration of 0.0008 mole of catalyst per 100 grams of acid.

In both the azeotropic and non-azeotropic methods the heating schedule is of extreme importance. Experimentation has indicated that the maximum temperature of 235°C. must be approached slowly over a period of one hour. It is suggested that the temperature reach 210-215°C. in the first half hour of heating and that the maximum temperature be reached by the end of the second half hour.

Since TMC has a relatively low melting point (131°C.), it enters into reaction with fatty acids with great facility. It is not volatile and does not cause foaming of the reaction mixture.

Similar procedures may be followed in the case of soybean, dehydrated castor, and other acids. As the unsaturation of the acids increases, the high functionality of TMC makes gelation possible unless this is guarded against by avoiding excessive temperatures and long heating schedules.

Film Properties

Drying tests were carried out on the linseed ester of TMC in order to determine the most effective drier combination. The TMC ester used was prepared with zinc stearate as a catalyst. Zinc was used since lead was known to be an effective drier. Zinc stearate, on the other hand, was very insoluble in the reconstituted oil; and, as may be seen in Table I, zinc was the most ineffective of all the driers tested. Likewise, comparative tests were performed with the linseed esters of glycerol and pentaerythritol. The metallic driers were in the form of octoates in solutions consisting of 80% xylene and 20% isobutanol. The oils were allowed to stand with the driers for at least 24 hours before 0.0015 inch films were cast on clean glass plates. Drying was allowed to proceed under ordinary laboratory conditions at about 74-78°C. The films were exposed to ordinary daylight and no artificial light was used at night. The films were examined at intervals by the finger tip method.

ESTERIFICATION OF ALCOHOLS WITH LINSEED ACIDS AT
235° C. CATALYZED BY URANYL STEARATE

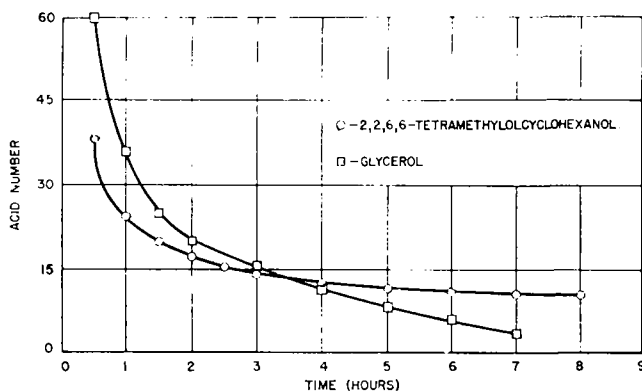


FIG. VIII

The following times were noted:

I. Initial set—

The film first becomes slightly sticky or tacky.

II. Set to touch—

None of the film is removed when touched with the finger.

III. Lint-free—

No lint is left on the film when it is brushed with cotton.

IV. Dried hard—

No imprint is left on the film when pressure is applied with the finger, or else the slight imprint which results may be removed easily by light polishing.

The drying times of the linseed ester of TMC of viscosity II (Gardner-Holdt standards) under the influence of various driers and drier combinations are indicated in Table I.

From these tests it is apparent that cobalt and lead comprise the most efficient drying combination. Manganese seemed to be of little value and in some cases actually exerted a negative effect. The best "through" dry was obtained with lead.

Comparative drying tests with the linseed esters of glycerol, pentaerythritol, and TMC were carried out according to the above-outlined conditions. All the oils were bodied to the same viscosities and had the following constants:

	Acid No.	Hydroxyl No.	Visc. at 25°C. (Gardner-Holdt)
Linseed Acid Ester of:			
Glycerol.....	10.3	10.4	H
Pentaerythritol.....	5.4	11.3	H
TMC.....	7.9	17.2	H

The glycerol ester was heat bodied to a viscosity of H from an original viscosity of B, whereas the pentaerythritol ester was bodied to H viscosity from an original viscosity of C. The TMC oil possessed a viscosity of II at the start.

The results of drying tests with three different drier combinations are indicated in Table II.

The best results were obtained for all the oils with the drier combination of cobalt and lead. Although the TMC and pentaerythritol oils reached the ultimate stage of dryness at approximately the same time, the TMC oil exhibited an advantage in that it dried faster initially in every case.

The TMC oil possessed a further advantage in that it dried to yield a harder film than either of the other two oils. The following pencil hardnesses were noted:

	Pencil Hardness	
	After 30 hours	After 72 hours
Linseed Acid Ester of:		
Glycerol.....	Softer than 6B	Softer than 6B
Pentaerythritol.....	5B	4B
TMC.....	3B	2B

In similar compositions prepared with soybean acids, TMC demonstrated the same sort of superior qualities.

Summary

It has been found that TMC may be esterified readily with linseed acids when 10% excess of alcohol is used. The optimum temperature of esterification is 235°C. The esterification is greatly facilitated by the use of catalysts such as lead stearate, with which an acid number of seven may be obtained in eight hours. Zinc stearate and uranyl stearate are likewise good catalysts, not only for the esterification of TMC but also for the esterification of glycerol.

When the linseed esters of glycerol, pentaerythritol, and TMC are compared it is found that the last exhibits the advantage of a faster initial drying time although the final drying times of the pentaerythritol and TMC esters are the same. Both dry considerably faster than glycerol. The TMC oil exhibits a further advantage in that it dries to the hardest film of all three oils. Results of a similar nature were obtained with soybean oil acid compositions.

Acknowledgment

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TABLE II
Drying Times for the Linseed Acid Esters of Polyhydric Alcohols

	Drier	Time (hours)			
		Initial Set	Set to Touch	Lint-free	Dried Hard
Linseed Acid Ester of:					
Glycerol.....	.03% cobalt + .25% lead	1.2	3.5	5.0	7.0
Pentaerythritol TMC.....	.03% cobalt + .25% lead	.80	1.9	2.3	4.0
	.03% cobalt + .25% lead	.66	1.3	2.0	4.0
Glycerol.....	.03% cobalt + .03% manganese	4.0	6.0	9.0	11.0
	.03% cobalt + .03% manganese	3.0	4.5	6.0	8.0
Pentaerythritol TMC.....	.03% cobalt + .03% manganese	3.0	4.0	4.5	8.0
	.03% cobalt + .25% calcium	1.2	2.8	3.8	7.0
Glycerol.....	.03% cobalt + .25% calcium	.90	1.8	2.3	5.0
	.03% cobalt + .25% calcium	.80	1.5	2.0	5.0