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3,206,405

SYNTHETIC LUBRICANTS COMPRISING DEHYDROCONDENSATION PRODUCTS OF POLYESTERS

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This invention relates to the art of lubrication. More particularly, it is concerned with synthetic type lubricating oils comprising dehydrocondensation products of certain poiesters.

As is well known, mineral oils, which for many years had provided satisfactory lubrication for piston-engined aircraft, have proved to be inadequate for jet engines, due to the extreme ranges of temperatures to which the oil is subjected in jet aircraft. This need has been met by the development of synthetic-type lubricating oils, particularly the esters of dibasic acids. The latest types of turbo-jet and turbo-prop engines, however, have forced bearing and oil temperatures higher, i.e., up to 550–600° F. In order to provide adequate lubrication for these newer engines, increased viscosity of the lubricating oil at these higher operating temperatures is required. At the same time, the viscosity-temperature characteristics of the oil must be such as to permit starting the engine at temperatures below at least about –30° F. Thus, the pour point of the oil must be below –30° F. or lower.

In accordance with the present invention, it has been found that conventional polyester lubricating oils when reacted with certain organic peroxides form dehydrocondensation products having high temperature viscosities which are substantially higher than those of the polyesters themselves. At the same time the low temperature viscosity levels and pour points of the products can be maintained within reasonable limits. Thus, it has also been found that the viscosities of the products can be controlled by the amount of peroxide employed in the dehydrocondensation reaction whereby the products are suitable either as lubricating oils, per se, or (in the case of highly viscous products) as blending agents for conventional ester-type oils to improve the viscosity-temperature characteristics thereof. Also, the products of the invention exhibit good shear-resistance as opposed to conventional polymeric oil addends. It is, therefore, the primary object of this invention to provide a novel class of lubricating oils comprising dehydrocondensation products of polyesters.

It is also an object to provide novel lubricating oil compositions comprising blends of conventional ester oils and dehydrocondensed polyesters.

Other objects and advantages of the invention will appear from the following detailed description thereof.

The polyesters which may be dehydrocondensed in accordance with the invention may be any polyester having an abstractable hydrogen atom. Thus, di-, tri- and tetraesters of di-, tri- and tetra-carboxylic acids and di-tri-, tetra- and polyesters of glycols, triols and polyhydric al-

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cohols may be employed. Non-limiting examples of suitable esters are the following:

Di-butyl phthalate
Di-octyl adipate
Di-2-ethylhexyl sebacate
Di-2-ethylhexyl azelate
Trimethylol propane trioctanoate
Trimethylol propane tridecanoate
Trimethylol butane hexanoate
Pentaerythrityl tetraoctanoate
Pentaerythrityl tetradecanoate

The organic peroxides utilizable in the invention may be any organic peroxide or hydroperoxide which breaks down on heating to give free radicals. However, tertiary alkyl peroxides containing from 8 to about 20 carbon atoms, such as di-t-butyl peroxide, di-t-amyl peroxide, t-amyl, t-butyl peroxide and di-t-octyl peroxide, are particularly suitable.

The dehydrocondensation reaction is carried out by intermixing from about 5 to about 50 weight percent of the peroxide with the ester and heating the mixture for a period of from about 1 to about 10 hours at a temperature of from about 100° C. to about 200° C. Free alcohol formed in the reaction is then removed by distillation. The reaction can be carried out in one step utilizing relatively large amounts of peroxide, i.e., 15–20% or more, or it can be conducted in stages using relatively small amounts, such as about 5%, and repeating the reaction with this amount several times until a product having the desired viscosity is obtained. The latter procedure is useful in determining the amount of peroxide which will provide a product having a certain viscosity from a particular polyester, while the former procedure is generally the one used after such a determination has been made.

A full understanding of the invention will be had by reference to the following illustrative examples.

EXAMPLE 1*Dehydrocondensation of di-2-ethylhexyl sebacate*

A mixture of 500 grams of di-2-ethylhexyl sebacate and 25 grams of di-t-butyl peroxide were reacted under reflux at 135–145° C. for 5 hours. Tertiary butyl alcohol, formed during the reaction, was removed by distillation. A 100-gram sample was then removed from the reaction mixture. The reaction mixture was then subjected to reaction with four additional portions of peroxide under the same conditions as in the original reaction, the portion of peroxide added in each instance amounting to approximately 5% of the remaining reaction mixture. Table I shows the physical properties of the products obtained in each of these reactions, numbered 1–5 in the table.

A separate reaction was also conducted under the conditions of the first of the preceding series of reactions, except that 18 weight percent of di-t-butyl peroxide was reacted all at once with the di-2-ethylhexyl sebacate. The properties of the product of this reaction (Reaction No. 6) are also given in Table I.

It will be seen from Table I that the viscosity of the dehydrocondensation product increases in proportion to the amount of peroxide employed in the reaction. How-

ever, the pour point of the products is not increased over that of the original ester.

TABLE I.—PROPERTIES OF DEHYDROCONDENSED DI-2-ETHYLHEXYL SEBACATE

	Unreacted polyester	Product of Reaction No. 1	Product of Reaction No. 2	Product of Reaction No. 3	Product of Reaction No. 4	Product of Reaction No. 5	Product of Reaction No. 6
KV at 400° F., cs.	1.08	1.24	1.48	1.77	2.07	2.23	2.00
KV at 210° F., cs.	3.31	4.12	5.22	6.75	8.81	9.65	8.32
KV at 100° F., cs.	12.67	17.30	24.43	34.88	50.17	56.81	45.78
KV at -40° F., cs.	1,426	2,625	4,969	9,364	17,740	22,340	14,910
ASTM slope	-0.71	-0.69	-0.66	-0.64	-0.61	-0.61	-0.62
Percent recovery per treat.	99.3	99.4	99.4	99.4	99.1	98.2	97.8
Flash point, COC, ° F.	465	450	450	455	460	450	440
API gravity	23.3	21.8	21.6	20.9	19.7	20.9	20.4
Neutralization No.	0.17	0.14	0.44	0.59	0.66	0.68	0.60
Pour point, ° F.	<-65	<-65	<-65	<-65	<-65	<-65	<-65

EXAMPLE 2

Dehydrocondensation of trimethylol propane trioctanoate

A mixture of 503 grams of trimethylol propane tri-
octanoate and 25 grams of di-t-peroxide were reacted under
reflux at 140–150° C. for 6 hours. Tertiary butyl
alcohol, formed during the reaction, was removed by dis-
tillation. A 100-gram sample was then removed from
the reaction mixture. The reaction mixture was then
subjected to reaction with three additional portions of
peroxide under the same conditions as the original reac-
tion. A sample of the reaction mixture (product) was
taken after each reaction. The portion of peroxide added
in each instance amounted to approximately 5%, by
weight, of the remaining reaction mixture. The physical
properties of the products of these four reactions are
given in Table II.

Here again, it is seen that the viscosities of the prod-
ucts are greater than those of the original ester and that
the viscosities increase in proportion to the amount of
peroxide used. At the same time, however, the pour
point of the products remains unchanged.

TABLE II.—PROPERTIES OF DEHYDROCONDENSED TRIMETHYLOL PROPANE TRIOCTANOATE

	Unreacted polyester	Product of Reaction No. 1	Product of Reaction No. 2	Product of Reaction No. 3	Product of Reaction No. 4
KV at 400° F.	1.12	1.37	1.66	2.13	2.81
KV at 210° F.	4.21	5.33	6.98	10.00	14.51
KV at 100° F.	19.60	28.42	41.62	65.42	113.8
KV at -40° F.	4,067	8,534	13,444	48,928	13.7
API gravity	36.8	15.9	15.3	14.1	1.2
Neutralization No.	0.10	0.76	1.1	1.2	1.2
Pour point, ° F.	<-30	<-30	<-30	<-30	<-30
Flash point, ° F.	470	480	485	495	500

EXAMPLE 3

Dehydrocondensation of trimethylol propane tripelargonate

In this example the trimethylol propane tripelargonate
was reacted for 6 hours with 15%, by weight, of di-t-
butyl peroxide at 135–150° C. The t-butyl alcohol
formed in the reaction was removed by distillation. The
properties of the original ester and the dehydrocondensate
product are shown in Table III.

TABLE III.—PROPERTIES OF DEHYDROCONDENSATE OF TRIMETHYLOL PROPANE TRIPELARGONATE

	Unreacted ester	Dehydrocon- densation product
KV at -40° F.	5,130	50,000
KV at 100° F.	24.13	116.2
KV at 210° F.	4.93	15.53
KV at 400° F.	1.42	3.11
Pour point, ° F.	-65	-55
Neutralization No.	0.01	0.28
Flash point, ° F.	525.0	530

EXAMPLE 4

Dehydrocondensation of "Hercolube 600"

A mixture 502 grams of "Hercolube 600" (a mixed
C₈-C₁₂ fatty acid ester of pentaerythritol) and 25 grams
of di-t-butyl peroxide were reacted under reflux at 140°
C. to 150° C. for 6 hours. Tertiary butyl alcohol, formed
during the reaction, was removed by distillation. A 100-
gram sample was removed from the reaction mixture.
The reaction mixture was subjected to 3 further reactions

as in Examples 1 and 2, i.e., by adding fresh portions of
peroxide amounting in each instance to about 5%, by
weight, of the reaction mixture after withdrawal of
samples. The physical properties of the products are
given in Table IV.

It is seen that as in Examples 1-3, the viscosities of
the products increase in proportion to the amount of
peroxide reacted with the ester. However, in this case
is noted that the pour point of the product of the fourth
peroxide reaction shows a rise over that of the ester.

TABLE IV.—DEHYDROCONDENSATION OF "HERCOLUMBE 600" (MIXED C₈-C₁₂ ACID ESTER OF PENTAERYTHRITOL)

	Unreacted polyester	Product of Reaction No. 1	Product of Reaction No. 2	Product of Reaction No. 3	Product of Reaction No. 4
KV at 400° F.	1.27	1.71	2.32	3.48	6.04
KV at 210° F.	4.95	7.45	11.46	20.21	41.63
KV at 100° F.	26.42	46.80	86.82	185.8	478.2
KV at -40° F.	8,160	28,787	100×10 ⁶	200×10 ⁶	6.4
API gravity	9.8	9.0	7.8	6.8	0.87
Neutralization No.	0.17	0.22	0.40	0.48	1.0
Pour point, ° F.	<-30	<-30	<-30	<-30	-10
Flash point, ° F.	495	515	515	500	515
Molecular weight	555	660	780	1,200	

EXAMPLE 5

Preparation of blending agent from "Hercolube 600"

"Hercolube 600" was refluxed with 25 weight percent of di-t-butyl peroxide at 140–150° C. for several hours. In the course of stripping the product, a gel was formed. Liquid product was extracted with toluene, in which the gel is insoluble. This material (extract) was used as a blending stock in di-2-ethylhexyl sebacate, trimethylol propane trioctanoate and "Hercolube 600." Properties of the blends, as well as Sonic Oscillator shear data, are given in Table V.

It will be seen that the dehydrocondensed ester is highly advantageous as a blending stock for the ester-type oils, since it substantially increases both the viscosity and viscosity index of the base ester oil. It is seen further than the 10% treated-ester blend does not significantly detract from the shear stability of the (di-2-ethylhexyl sebacate) oil.

Results similar to those shown in Table V are attained with blends of the products in conventional ester oils other than di-2-ethylhexyl sebacate. As is well known, these ester oils are derived from either (a) monohydric aliphatic alcohols, such as butyl, iso-butyl, octyl, decyl, dodecyl and tetradecyl alcohol, and aliphatic dicarboxylic acids, such as adipic, pimelic, suberic, azelaic and sebacic acid, or (b) polyhydric alcohols, such as ethylene glycol, trimethylol propane, trimethylol butane, pentaerythritol, etc., and monocarboxylic acids, such as acetic, valeric, decanoic, myristic, stearic, etc.

TABLE V.—PROPERTIES OF "HERCOLUMBE 600" DEHYDROCONDENSATE¹ BLENDS

Base fluid	Dehydrocondensate, wt. percent	KV at -40° F.	KV at 100° F.	KV at 210° F.	VI
Di-2-ethylhexyl sebacate.....	0	1,426	12.55	3.31	154
	5	2,155	18.02	4.58	185
	10	3,225	25.46	6.23	173
	15	5,079	36.23	8.55	166
Trimethylol propane trioctanoate.....	0	4,067	19.60	4.21	139
	5	6,435	28.09	5.74	151
	10	10,140	40.18	7.48	152
	15	15,042	57.75	11.01	150
"Hercolube 600".....	0	8,160	26.42	4.95	129
	5	14,180	39.06	7.21	143
	10	23,111	56.45	9.86	143
	15	39,596	83.21	13.98	143

Sonic Oscillator Shear Test:²

Sample=10 wt. percent of "Hercolube 600" dehydrocondensate in di-2-ethylhexyl sebacate.

KV at 210° F. Original=6.23

Final=5.02

Percent Change=-5

(1) "Hercolube 600" dehydrocondensate: KV at 210° F.=748.6.

(2) ASTM Proposed Test Method, Preprint 35-S, 1961, Appendix XII, page 61.

EXAMPLE 6

Dehydrocondensation of fluoroalkyl camphorate

A mixture of 202 grams of Du Pont Stable Lubricant No. 316, a fluoroalkyl camphorate (a diester of camphoric acid and the fluoro alcohol, $H(CF_2)_6CH_2OH$) and 18 grams of di-t-butyl peroxide was refluxed for 16 hours. Light products were removed by distillation and unreacted starting material was removed by vacuum distillation. The yield of product was 37 grams (18.5% based on the starting ester). The properties are given in Table VI. It will be seen that the product has a viscosity and flash point substantially higher than the original ester.

TABLE VI.—PROPERTIES OF FLUOROALKYL CAMPHORATE DEHYDROCONDENSATION PRODUCT

	Unreacted ester	Dehydrocondensation product
KV at 100° F.....	115.5	8,114
KV at 210° F.....	8.22	97.96
Flash point, ° F.....	460	525

As shown in Tables I–IV, the neutralization number (N.N.) of the dehydrocondensation product in some instances is slightly higher than that of the starting polyester. However, this increase in N.N. can be eliminated by simple percolation over a suitable adsorbent, such as alumina or florisil.

Table VII shows the results obtained by the percolation treatment of a dehydrocondensed trimethylol propane tripelargonate ester. It will be seen that the product which was not subjected to percolation had an N.N. of 0.28, but that the N.N. of the percolated product with or without thermal treatment (columns 2 and 3) was lowered to substantially that of the original ester.

It has been found also that reaction of the starting ester with over about 10%, by weight, of peroxide provides a product of somewhat lower thermal stability than that of the starting ester. However, this may be overcome by subjecting the product to a simple thermal treatment. This involves simply heating the product to a temperature of, say, 400–600° F. in a nitrogen atmosphere. Table VIII shows the effect of the thermal treatment on the thermal stability of a dehydrocondensed trimethylol alkane tripelargonate. It will be seen from the table that percolation alone has only a minor effect on the thermal stability of the product, while heat-treating results in a large improvement in thermal stability. Percolation used after heat-treating removes acidic decomposition products and improves the color of the product.

TABLE VII.—EFFECT OF THERMAL TREATMENT AND/OR PERCOLATION ON PHYSICAL PROPERTIES OF DEHYDROCONDENSED TRIMETHYLOL PROPANE TRIPELARGONATE

	15% di-t-butyl peroxide reaction product		
	No treatment	Percolated	Thermally-treated and percolated ¹
KV at -40° F.....	50,000	-----	30,000
KV at 100° F.....	116.2	100.6	60.24
KV at 210° F.....	15.53	14.44	9.48
KV at 400° F.....	3.11	-----	2.1
Pour point, ° F.....	-55	-----	<-65
Neutralization No.....	0.28	0.00	0.05
Flash point, ° F.....	530	-----	525

¹ Heated at 536° F. for 24 hours under nitrogen and percolated over clay and alumina.

TABLE VIII.—THERMAL STABILITY¹ OF TREATED AND UNTREATED DEHYDROCONDENSED TRIMETHYLOL PROPANE TRIPELARGONATE

	15% di-t-butyl peroxide reaction product		
	No treatment	percolated	Thermally treated and percolated ²
Weight loss, percent change.....	0.3	0.0	0.4
KV at 100° F., percent change.....	-29.7	-23.2	+3.3
KV at 210° F., percent change.....	-24.7	-22.0	+0.8
Neutralization Number.....	2.5	1.6	0.9

¹ Test Method: Sample heated to 536° F. in nitrogen atmosphere for 24 hours.

² Heated at 536° F. for 24 hours under nitrogen and percolated over clay and alumina.

It will be seen that the invention (1) provides polyester dehydrocondensation products having viscosities and low temperature characteristics which make them desirable lubricating oils for high temperature application, such as jet engine lubricants and (2) that these products are highly advantageous blending agents for conventional ester lubricating oils. It will be understood that the amount of the dehydrocondensation product added to an ester base oil can vary over a wide range, depending upon the viscosity of the particular product used and the viscosity desired in the finished blend. Thus, the products, being lubricating oils of themselves, may comprise either

a major or a minor proportion of the finished oil blends. From the standpoint of increasing the viscosity and/or viscosity index of the ester-base oil, however, the amount of dehydrocondensation product employed will generally be no greater than about 40 weight percent and may be as little as 1 weight percent, based on the total composition.

The lubricating oil compositions of the invention may contain additives normally added to lubricating oil for the purpose of improving the various characteristics thereof, such as antioxidants, detergents, extreme pressure agents, anti-wear agents, metal deactivators, etc.

Although the invention has been illustrated herein by means of specific examples and embodiments thereof, it is not intended that the scope of the invention be limited in any way thereby except as defined in the following claims.

We claim:

1. A lubricating oil comprising a dehydrocondensation product prepared by reacting (a) a polyester derived from a carboxylic acid, selected from the group consisting of mono- and polycarboxylic acids, said acids containing from about 2 to about 20 carbon atoms exclusive of carboxyl carbons, and an alcohol, selected from the group consisting of mono- and polyhydroxy alcohols, said alcohol containing from about 2 to about 20 carbon atoms with (b) from about 5% to about 50%, by weight, based on the polyester, of a di-tertiary alkyl peroxide containing from about 8 to about 20 carbon atoms, at a temperature of from about 100° C. to about 200° C. to form a dehydrocondensation product of said polyester and removing free alcohol formed in the reaction from the dehydrocondensation product.

2. A lubricating oil comprising a dehydrocondensation product prepared by reacting di-2-ethylhexyl sebacate with from about 5% to about 50%, by weight, based on the weight of the di-2-ethylhexyl sebacate, of di-tertiary-butyl peroxide, at a temperature of from about 100° C. to about 200° C., to form a dehydrocondensation product of di-2-ethylhexyl sebacate and removing free di-tertiary-butyl alcohol formed in the reaction from the dehydrocondensation product.

3. A lubricating oil comprising a dehydrocondensation product prepared by reacting trimethylol propane trioctanoate with from about 5% to about 50%, by weight, based on the weight of the trimethylol propane trioctanoate, of di-tertiary-butyl peroxide, at a temperature of from about 100° C. to about 200° C., to form a dehydrocondensation product of trimethylol propane trioctanoate and removing free di-tertiary-butyl alcohol formed in the reaction from the dehydrocondensation product.

4. A lubricating oil comprising a dehydrocondensation product prepared by reacting trimethylol propane tripelargonate with from about 5% to about 50%, by weight, based on the weight of the trimethylol propane tripelargonate, of di-tertiary-butyl peroxide, at a temperature of from about 100° C. to about 200° C., to form a dehydrocondensation product of trimethylol propane tripelargonate and removing free di-tertiary-butyl alcohol formed in the reaction from the dehydrocondensation product.

5. A lubricating oil comprising a dehydrocondensation product prepared by reacting a mixed C₈-C₁₂ carboxylic acid ester of pentaerythritol with from about 5% to about 50%, by weight, based on the weight of said ester, of di-tertiary-butyl peroxide, at temperature of from about 100° C. to about 200° C., to form a dehydrocondensation product of the mixed C₈-C₁₂ carboxylic acid ester of pentaerythritol and removing free di-tertiary-butyl alcohol formed in the reaction from the dehydrocondensation product.

6. A lubricating oil composition comprising a blend of a conventional ester oil and a dehydrocondensation product prepared by reacting (a) a polyester derived from a carboxylic acid, selected from the group consisting of

mono- and polycarboxylic acids, said acids containing from about 2 to about 20 carbon atoms exclusive of carboxyl carbons, and an alcohol, selected from the group consisting of mono- and polyhydroxy alcohols, said alcohol containing from about 2 to about 20 carbon atoms with (b) from about 5% to about 50%, by weight, based on the polyester of a di-tertiary alkyl peroxide containing from about 8 to about 20 carbon atoms, at a temperature of from about 100° C. to about 200° C. to form a dehydrocondensation product of said polyester and removing free alcohol formed in the reaction from the dehydrocondensation product.

7. A lubricating oil composition comprising a blend of a conventional ester oil and a dehydrocondensation product prepared by reacting di-2-ethylhexyl sebacate with from about 5% to about 50%, by weight, based on the weight of the di-2-ethylhexyl sebacate, of di-tertiary-butyl peroxide, at a temperature of from about 100° C. to about 200° C., to form a dehydrocondensation product of di-2-ethylhexyl sebacate and removing free di-tertiary-alcohol formed in the reaction from the dehydrocondensation product.

8. A lubricating oil composition comprising a blend of a conventional ester oil and a dehydrocondensation product prepared by reacting trimethylol propane trioctanoate with from about 5% to about 50%, by weight, based on the weight of the trimethylol propane trioctanoate, of di-tertiary-butyl peroxide, at a temperature of from about 100° C. to about 200° C., to form a dehydrocondensation product of trimethylol propane trioctanoate and removing free di-tertiary-butyl alcohol formed in the reaction from the dehydrocondensation product.

9. A lubricating oil composition comprising a blend of a conventional ester oil and a dehydrocondensation product prepared by reacting trimethylol propane tripelargonate with from about 5% to about 50%, by weight, based on the weight of the trimethylol propane tripelargonate, of di-tertiary-butyl peroxide, at a temperature of from about 100° C. to about 200° C., to form a dehydrocondensation product of trimethylol propane tripelargonate and removing free di-tertiary-butyl alcohol formed in the reaction from the dehydrocondensation product.

10. A lubricating oil composition comprising a blend of a conventional ester oil and a dehydrocondensation product prepared by reacting a mixed C₈-C₁₂ carboxylic acid ester of pentaerythritol with from about 5% to about 50%, by weight, based on the weight of said ester, of di-tertiary-butyl peroxide, at a temperature of from about 100° C. to about 200° C., to form a dehydrocondensation product of the mixed C₈-C₁₂ carboxylic acid ester of pentaerythritol and removing free di-tertiary-butyl alcohol formed in the reaction from the dehydrocondensation product.

11. A lubricating oil as defined in claim 1 which has been improved as to its thermal stability by heating to a temperature of from about 400° F. to about 600° F. in a nitrogen atmosphere.

12. The lubricating oil composition of claim 6, wherein the amount of dehydrocondensation product blended with the conventional ester oil is from about 1% to 40%, by weight, of total composition.

13. A lubricating oil comprising a dehydrocondensation product prepared by reacting a polyester having an abstractable hydrogen atom with from about 5% to about 50%, by weight, based on the polyester, of a di-tertiary alkyl peroxide containing from about 8 to about 20 carbon atoms, at a temperature of from about 100° C. to about 200° C. to form a dehydrocondensation product of said polyester and removing free alcohol formed in the reaction from the dehydrocondensation product.

14. A lubricating oil composition comprising a blend of a conventional ester oil and a dehydrocondensation product prepared by reacting a polyester having an abstractable hydrogen atom with from about 5% to about 50%, by weight, based on the polyester of a di-tertiary

alkyl peroxide containing from about 8 to about 20 carbon atoms, at a temperature of from about 100° C. to about 200° C. to form a dehydrocondensation product of said polyester and removing free alcohol formed in the reaction from the dehydrocondensation product.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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Herbert L. Hepplewhite et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 21, for "di-t-peroxide" read -- di-t-butyl peroxide --; column 6, TABLE VII, in the heading to columns 2, 3 and 4, for "15% di-t-butyl perTxide" read -- 15% di-t-butyl peroxide --; column 8, line 25, for "preparted" read -- prepared --.

Signed and sealed this 24th day of May 1966.

(SEAL)

Attest:

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