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LUBRICANT COMPOSITION

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No Drawing. Continuation-in-part of application Ser. No. 800,006, Feb. 17, 1969. This application Jan. 11, 1971, Ser. No. 105,603

Int. Cl. C10m *1/26, 1/34*

U.S. Cl. 252—51.5 A 6 Claims

ABSTRACT OF THE DISCLOSURE

Lubricant compositions comprising fatty acid diesters of tripropylene glycol wherein each fatty acid moiety contains from about 6 to about 10 carbon atoms and, as an antioxidant from about 0.001% to about 5% of a mixture of p,p'-dioctyldiphenylamine and N-phenyl-1,2,3,4-tetrahydro-2-naphthylamine.

REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of my copending application Ser. No. 800,006 filed Feb. 17, 1969, now abandoned, for Lubricant Composition.

The disclosure of fatty acid diesters of tripropylene glycol wherein said fatty acids contain from about 6 to about 10 carbon atoms as lubricating base fluids can be found in the copending application of Edward J. Conklin and Paul K. Platt, Ser. No. 799,908, entitled Lubrication Process, filed Feb. 17, 1969 and now abandoned.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to lubricant compositions comprising a unique lubricating base fluid and an antioxidant. These lubricant compositions have acceptable flash points, freezing points and load-bearing characteristics for use as jet engine lubricants.

(2) Prior art

Dipropylene glycol dipelargonate has been sold as a base fluid for synthetic lubricant compositions. This material has a flash point which is too low for use in, e.g., jet engine lubricant compositions since at high temperatures too much of the fluid would be lost by evaporation. Also, although dipropylene glycol dipelargonate has a very low pour point, it solidifies when held at temperatures where it must remain fluid.

THE INVENTION

This invention relates to lubricant compositions comprising fatty acid diesters of tripropylene glycol wherein each fatty acid moiety contains from about 6 to about 10 carbon atoms, preferably from 7 to 9 carbon atoms, and from 0.001% to about 5% of an antioxidant which is a mixture of p,p'-dioctyldiphenylamine and N-phenyl-1,2,3,4-tetrahydro-2-naphthylamine.

THE TRIPROPYLENE GLYCOL DIESTER

The unique lubricating base fluid of this composition is a fatty acid diester of tripropylene glycol. Fatty acid diesters of dipropylene glycol have flash points which are too low for use as lubricants for the latest jet engines and both the dipropylene glycol and tetrapropylene glycol diesters become solid when held at low temperatures, e.g., about —65° F. Furthermore, diester of tripropylene glycol which contain two fatty acid residues containing about 6 carbon atoms or less will degrade under extreme temperature conditions and esters containing fatty acids having 10 or more carbon atoms will tend to have pour points which are too high. Therefore, for use as a jet

engine lubricant, it is required that one use diesters of tripropylene glycol wherein the fatty acids contain from about 6 to about 10 carbon atoms and only minor amounts of the fatty acids contain either 6 or 10 carbon atoms. Some small amounts of C_{11} and higher fatty acids can be present in the diesters, but in general they should be avoided. Synthetic fatty acids can also be used.

Suitable tripropylene glycol diesters are disclosed hereafter in the examples. Other lubricating base fluids can also be used in combination with the specific unique lubricating base fluid of this invention. Suitable base fluids are disclosed in the copending application of Robert E. Wann, Denzel Allan Nicholson and Ted Joe Logan entitled Lubricant Composition filed Sept. 26, 1968, Ser. No. 762,966, now U.S. Pat. 3,579,449. This application is incorporated herein by reference.

The tripropylene glycol diester lubricating base fluid of this invention seems to be too unstable for use by itself in the high temperatures of the latest jet engines because of the hydrogen atom which is attached to a tertiary carbon atom in the tripropylene glycol chain. Accordingly, in order for the tripropylene glycol diester to be used in a jet engine lubricant one must also include an effective antioxidant.

THE ANTIOXIDANT

Antioxidants are well known lubricant additives. The preferred antioxidant package is a mixture of p,p'-dioctyldiphenylamine and N-phenyl-1,2,3,4-tetrahydro-2-naphthylamine.

The p,p'-dioctyldiphenylamine is a known antioxidant and is a readily available article of commerce. The other antioxidant of the package, N-phenyl 1,2,3,4-tetrahydro-2-naphthylamine, can be readily prepared by reacting 1,2,3,4-tetrahydro-2-naphthol, a known compound whose preparation is described in Brochet et al., Bull. Soc. Chim., 31, 1280–85 (1922), with aniline according to the general procedure for reacting amines with hydroxyl compounds as described by Guyot et al., Bull. Soc. Chim., 47, 203–10 (1930).

The N-phenyl-1,2,3,4-tetrahydro-2-naphthylamine shall make up from about 30% to about 80% of the mixture, preferably from about 50% to about 70%. It is preferred that these two amines be used in a ratio of two parts of p,p'-dioctyldiphenyl amine to three parts N-phenyl-1,2,3,4-tetrahydro-2-naphthylamine. A preferred level of the antioxidant is about 1.5% by weight of the lubricant composition and a preferred range is from about 0.1% to about 2%.

It is believed that the p,p'-dioctyldiphenylamine acts (1) as a free radical inhibitor, (2) as a dispersant, and (3) in a secondary role as a base. It is believed that the N-phenyl-1,2,3,4-tetrahydro-2-naphthylamine acts primarily as a base to neutralize any acid produced either in storage or in use. Other materials serving the same functions can be substituted either wholly, or in part, for the above mentioned components of the antioxidant mixture.

OTHER LUBRICANT ADDITIVES

Among the additional additives which can be added to the compositions of this invention include viscosity index improvers, pour point depressants, dispersants, antiware additives, metal deactivators, etc.

The viscosity index improvers are normally used at a level from about 0.01% to about 2% by weight of the lubricant composition. Suitable examples include polyisobutenes, polymethacrylates, vinylacetate-fumaric acid ester copolymers, and polyacrylates.

The pour point depressants are used at a level of from about 0.01% to about 2% by weight of the lubricant composition. Suitable pour point depressants are the aforementioned viscosity index improvers, alkylated

waxes, naphthalenes, polymethacrylates and alkylated wax phenols.

The metal deactivators (anticorrosion additives) are normally used at a level of from about 0.001% to about 0.5% by weight of the lubricant composition. Suitable metal deactivators include: disalicylidene-1,2-diaminepropane, benzoguanamine and N-alkyl and ring alkyl-substituted benzoguanamines; thioureas; octadecyl amine; quinizarin; quinolines; phenylacridine; hexamethylenetetramine; thiobenzamide; benzothiazole; and imidazoline.

The anti-wear additives are normally used at a level of from about 0.01% to about 5% by weight of the lubricant composition. Suitable anti-wear additives include tricresylphosphate, organic phosphites, and those long chain methylenediphosphonate esters disclosed in the aforementioned copending application of Robert Earl Wann, Denzel Allan Nicholson and Ted Joe Logan entitled Lubricant Composition filed Sept. 26, 1968.

Dispersants are normally used at a level of from about 0.01% to about 2% by weight of the lubricant composition. Suitable dispersants include: The aforementioned viscosity index improvers; copolymers of methacrylates or acrylates; N-substituted long chain alkenyl succinimides; high molecular weight esters or polyesters; and vinyl-acetate-fumaric acid ester copolymers.

Other suitable additives are disclosed in Canadian Pat. 792,739 which is incorporated herein by reference.

OTHER LUBRICATING BASE FLUIDS

The essential fatty acid diesters of tripropylene glycol can be combined with other known lubricating base fluids to improve their properties. Broadly, the other base fluid can be either a petroleum hydrocarbon, a fatty acid triglyceride, a synthetic fluid, an aqueous based fluid, or mixtures thereof. Petroleum hydrocarbons include mineral oil (including light solvents, neutral oils, heavy, bright and refined stocks, and asphaltic residual stocks), greases and waxes. The lubricating base fluid can also comprise suspensions of graphite in oils. Synthetic fluids include such disparate materials as polymerized olefins, organic carbonates, organic esters and/or ethers, polyglycols, silicones, modified organic materials (halogenated, phosphated, sulfurized, etc.) polymers, e.g., alkylmethacrylate polymers and synthetic resins, e.g., resins formed by esterification of polyhydric alcohols with polycarboxylic acids. Examples of base fluids which can be used in the practice of this invention include those disclosed in U.S. Pat. 2,599,761, especially columns 9–11; U.S. Pat. 2,725,359, especially columns 2, and 7–8; U.S. Pat. 2,767,142, especially column 4; U.S. Pat. 2,882,228, especially columns 6–7; U.S. Pat. 2,956,952, especially columns 3–5; U.S. Pat. 2,993,859, especially columns 2–3; U.S. Pat. 3,296,138, especially columns 6–10 and 12–20; and U.S. Pat. 3,357,920, especially columns 5–7. Other suitable lubricating base fluids are disclosed in "Encyclopedia of Chemical Technology," Kirk-Othmer, second edition, vol. 12, pp. 557–616, especially pp. 576–582, Interscience Publishers, 1967. More examples of metal working lubricant base fluids can be found in "Metal Working Lubricants," E. L. H. Bastian, first edition, McGraw-Hill Book Co., Inc., 1951. All of the above patents and books including the references referred to therein are incorporated herein by reference.

Especially preferred in such mixtures are (1) other esters of polyols and monobasic acids such as C_6–C_{12} fatty acid polyesters of ethylene glycol, polyethylene glycols, propylene glycol, other polypropylene glycols, neopentyl glycol, trimethylol ethane, trimethylol propane, and pentaerythritol; (2) dibasic acid esters, such as C_6–C_{12} fatty alcohol (including normal, branched and secondary alcohols) esters of adipic, azelaic, and sebacic acids; and (3) complex esters such as polyalkylene glycol dibasic acid polyesters terminated with either a monobasic acid or a monohydric alcohol.

Two types of lubricating base fluid mixtures are of special importance. These are fluids which are designed to meet military specifications MIL–L–7808G and MIL–L–23699A. The first specification (MIL–L–7808G) requires a low pour point and good wear characteristics. The C_6–C_{10} fatty acid diesters of tripropylene glycol are superior lubricating base fluids for preparing lubricant compositions to meet this specification which requires a low pour point and good wear characteristics. However, small amounts, usually less than 50% of some of the diesters of dibasic acids, e.g., dioctyl adipate or di(2-ethylhexyl) sebacate can be used in combination with the superior tripropylene glycol diesters. The resulting lubricant compositions can be more economical although they will not be as good as lubricant compositions containing only the tripropylene glycol diesters.

The second specification (MIL–L–23699A) requires a lower rate of evaporation, a higher viscosity, and a higher degree of thermal stability than can be obtained with the tripropylene glycol diester by itself. However, if small amounts, usually less than about 50% of the tripropylene diesters are added to such fluids as trimethylol propane tripelargonate or pentaerythritol tetraesters such as those described in U.S. Pat. 3,360,465 (incorporated herein by reference), one can lower the pour point of the lubricating composition and improve its wear characteristics without increasing the evaporation rate and decreasing viscosity to an unacceptable degree.

USES FOR THE LUBRICANT COMPOSITIONS

These compositions are uniquely adapted for use in the latest jet engines as lubricants. These compositions as well as longer chain acid esters are also capable of being used with improved results as automotive crankcase lubricants, transmission fluids, low temperature greases, lubricants for sintered bearings, steam turbine engine lubricants, textile lubricants, metal polishing lubricants (especially aluminum), brake fluids, metal working lubricants, lubricants for vacuum pumps, lubricants for two and four cycle engines, e.g., lawn mowers, lubricants for sealed lubricant systems, hydraulic fluids in general, and automotive and truck turbine engines.

The following examples are illustrative of the invention and should not be taken as limiting the scope of the invention.

EXAMPLE I

N-phenyl-1,2,3,4 tetrahydro-2-naphthyl amine is prepared in the following manner. 75 grams of active nickel catalyst is prepared by reduction of nickel oxide with hydrogen at 300° C. The 75 grams of catalyst is mixed with 1100 grams (7.5 moles) 1,2,3,4-tetrahydro β-napthol and 750 grams (8 moles) of aniline and the mixture is reacted under agitation in an autoclave at 180° C. and 20 kg./sq. cm. pressure for approximately three hours. The reaction mixture is then removed from the autoclave, filtered to remove the nickel catalyst, and acidified with dilute sulfuric acid. The aqueous solution containing the protonated product and aniline is extracted three times with diethyl ether to remove unreacted 1,2,3,4-tetrahydro β-napthol. The aqueous solution is then made basic with dilute NaOH and extracted three times with petroleum ether to give a petroleum ether solution of crude N-phenyl-1,2,3,4-tetrahydro-2-naphthylamine contaminated with small quantities of aniline. The latter is removed by multiple washing of the petroleum ether solution with cold H_2O. The petroleum ether solution is then dried with $MgSO_4$, filtered and cooled to give crystals of the desired product, M.P. 121–125 C.

EXAMPLE II

In this and the subsequent examples, all pour points are determined according to ASTM D97. The corrosion and oxidation stability tests were a modification of the Federal standard 791, Method 5308 wherein the tests were run at 347° F. The evaporation test was ASTM D972.

The following compares a tripropylene glycol diester wherein the fatty acids have the following approximate distribution C_6—4%; C_8—55%; C_{10}—40%; and C_{12}—1% and the same tripropylene glycol diester in a lubricant composition containing 1.5% of an antioxidant package which is a 40% p,p'-dioctyldiphenylamine and 60% N-phenyl-1,2,3,4-tetrahydro-2-naphthylamine.

	A. Oxidation-corrosion test (347° F.)							
	(1) Percent volume loss	(2) Total acid number	(3) Corrosivity (weight loss mg./cm.²) Al	Mg	Cu	Steel	Ag	B. Percent evaporation [1]
Tripropylene glycol diester (TPG)	23	24	Too bad to run					57
Tripropylene glycol diester and antioxidant package	2	0.55	0.000	0.008	0.188	0.015	0.008	15

[1] 6½ hours at 400° F.

The TPG alone lost an excessive amount of material in both the oxidation-corrosion and evaporation tests and the acid value became excessive while with the antioxidant system there was minimal loss in both tests and the acid value was acceptable. It can be seen from the above data that, surprisingly, the antioxidant is essential to the good performance of the composition in corrosivity, evaporation, and acid number.

Pour points were determined for various diesters of polyalkylene glycols as follows.

Diester:	Pour point (° F.)
(1) Tripropylene glycol dilaurate	—25
(2) Tripropylene glycol dicaprate	—59
(3) Tripropylene glycol dipelargonate	—90
(4) Tripropylene glycol dicaprylate	—100
(5) Tripropylene glycol diheptanoate	—100
(6) 50:50 mixture of (2) and (4)	—80
(7) Tripropylene glycol diester wherein the fatty acyl content, randomly distributed, is approximately 4% C_6; 55% C_8; 40% C_{10} and 1% C_{12}	—89
(8) (3) prepared with synthetic fatty acids	—85
(9) Tripropylene glycol diester with random C_9 fatty acids	—65
(10) Diethylene glycol dipelargonate	35
(11) Diethylene glycol dipelargonate (prepared from synthetic fatty acids)	—10
(12) Triethylene glycol dipelargonate	15
(13) (12) prepared with synthetic fatty acids	—5
(14) Tetraethylene glycol dipelargonate	25
(15) (14) prepared with synthetic fatty acids	—20
(16) Tripropylene glycol dibenzoate	0
(17) Dipropylene glycol dicaprate	—75
(18) Tetrapropylene glycol diester (n-C_8–C_{10} fatty acids—average $C_{8.6}$	—55
(19) Tripropylene glycol diester (n-C_8–C_{10} fatty acids—average $C_{8.6}$)	—85

When diesters (17), (18), and (19) were held at —65° F. for 72 hours, both (17) and (18) became solid whereas diester (19) retained a viscosity of about 9200 centipoises. This shows unusual low temperature viscosity stability for the diesters of this invention as compared with the dipropylene glycol and tetrapropylene glycol analogs. In Shell four ball tests at 40 kg. weight and 130° F. (17–19) gave acceptable wear scars of 0.57, 0.54, and 0.51 respectively. (17–19) were acceptable in Ryder Gear tests also, giving values of 2100, 2500, and 2900 p.p.i. respectively. These materials also had viscosity indices of 130, 143, and 30 respectively.

As can be seen from the above data many compounds which are quite similar to the essential tripropylene glycol diesters of this invention have surprisingly higher pour points despite the fact that the diesters of this invention have higher molecular weights. It is surprising that the diesters of this invention have so many of the good properties required for base fluids to be used to prepare lubricant compositions suitable for use in the most advanced jet engines.

It will be noted that the poor points for diesters of tripropylene glycol are lower than the corresponding diesters of dipropylene glycol, tetrapropylene glycol and polyethylene glycols.

EXAMPLE III

The following are excellent lubricant compositions. The antioxidant in each composition is the antioxidant mixture of Example I.

Composition	Base fluid	Percent antioxidants
(1)	Tripropylene glycol diesters containing fatty acyl groups having the following approximate random distribution: 4% C_2, 55% C_8, 40% C_{10} and 1% C_{12} (TPGDE).	2.0
(2)	Tripropylene glycol dipelargonate (TPGDP)	2.5
(3)	Tripropylene glycol dicaprylate (TPGDC)	1.5
(4)	Tripropylene glycol diheptanoate (TPGDH)	3.0
(5)	Tripropylene glycol dicaprate (TPGD Caprate)	1.8
(6)	1:1 mixture of TPGDP and TPGDC	2.6
(7)	30% TPGDE and 70% trimethylol propane tripelargonate (TPT).	2.0
(8)	40% TPGDE and 60% pentaerythritol tetraester containing 20% C_5, 45% C_8, 15% C_9 and 20% C_{10} acyl groups (PTE).	1.5
(9)	20% TPGDE, 30% TPT and 50% PTE	3.2
(10)	70% TPGDE and 30% dioctyl adipate	2.9
(11)	80% TPGDE and 20% di(2-ethylhexyl) sebacate	4.1
(12)	35% TPGDE and 65% of the condensation product of polyethylene glycol (n=4) and adipic acid terminated with 2-ethylhexanol (ATCE).	3.0
(13)	25% TPGDE and 75% of the condensation product of sebacic acid and polyethyleneglycol (n=5) terminated with pelargonic acid (PTCE).	2.6
(14)	20% TPGDE, 50% PTE, and 30% PTCE	2.4
(15)	20% TPGDE, 50% PTE, and 30% ATCE	1.8
(16)	30% TPGDE and 70% of the condensation product of sebacic acid and polypropylene glycol (n=3) terminated with caprylic acid (CTCE).	1.6
(17)	TPGDE	2.4
(18)	80% TPGDE and 20% dinonyl adipate	2.2

EXAMPLE IV

The following are excellent lubricant compositions. The named additives are added to the composition of Example I, replacing an equivalent amount of base fluid.

Composition	Additive	Percent additive
1	Disalicylidene-1,2-diaminepropane	.01
2	Benzoquanamine	.009
3	Thiorurea	.312
4	N-butylbenzoquanamine	.214
5	Octadecyl amine	.12
6	Quinazarin	.025
7	Quinoline	.4
8	Phenylacridine	.3
9	Hexamethylenetetramine	.24
10	Thiobenzamide	.16
11	Benzothiazole	.28
12	Imidazoline	0.111
13	1:10 mixture of benzoguanamine and tetraoctadecyl methylenediphosphonate.	2.2
14	1:10 mixture of quinazarin and tricresylphosphate	4.4
15	1:1 mixture of quinoline and naphthalene	0.8
16	Polymer of methacrylic acid esters (Acryloid 704)	0.5
17	Polymer of methacrylic acid esters (Acryloid 714)	0.6

EXAMPLE V

The following are excellent lubricant compositions. The named base fluids are substituted in the indicated amounts for the base fluid of Example I.

Composition	Base fluid	Percent
1	Allyl laurate	10
2	Propyl propionate	15
3	Trioctyl phosphate	20
4	Dioctyl carbonate	10
5	Isopropyl myristate	20
6	Stearyl acetate	25
7	Dibutyl ether of ethylene glycol	5
8	Glycerol	5
9	Napthalene	6
10	Petrolatum	10
11	Paraffin wax	10
12	1:1 mixture of naphthalene and xylene	7
13	Dioctylphthalate	8.5
14	Propylene glycol	7.2
15	Methyl ethyl ketone	4.6
16	Carnauba wax	9.2
17	Tallow	4.1
18	Stearyl alcohol	12.5
19	20% emulsion of tallow in water	90
20	Octyl tripropylene glycol ether	24
21	Mineral oil S.A.E. 10	13.1
22	Rosin	2.6
23	1:1 phenol-formaldehyde resin (M.W. 1,200)	4.7
24	Grease (lubricating oil thickened with soap)	8.6
25	Isopropyl laurate	22
26	1:1 mixture of isopropyl and alcohol	3
27	Kerosene	14
28	Turbine oil	12.9
29	40% soybean oil in water emulsion	80
30	Di(2-ethylhexyl)sebacate	21
31	10% suspension of graphite in mineral oil S.A.E. 10	70
32	Polyethyleneglycol (M.W. 1,800)	40
33	Polypropyleneglycol (M.W. 2,200)	30
34	Octyl ether of polyethyleneglycol (M.W. 4,000)	28
35	Di-2-ethylhexanoate of 1:1 ethylene glycol propylene glycol (M.W. 6,000).	8.9
36	Stearyl stearate	11
37	20% cottonseed oil in water emulsion with 5% alkyl(C_{11-15}) poly ethoxylate (9 moles) emulsifier.	70
38	Winterized and hardened (I.V. 8) soybean oil	8
39	Naphthenic hydrocarbon oil	14
40	Fluorinated polypropylene (M.W. 1,000)	10
41	Di-n-butylphthalate	4
42	1:1 mixture of di (2-butoxyethyl) azelate and di-(methylcyclohexyl)adipate.	20
43	The condensation product of propylene glycol, ethylene glycol, phthalic acid and sebacic acid in a 3:2:1:1: ratio (M.W. 2,000)	25
44	The C_8-C_{10} Oxo alcohol esters of phthalic acid	26
45	Butyl ether of polyethylene glycol (M.W. 1,000)	9
46	A 3:1 mixture of butyl ether of polypropylene glycol (M.W. 1,600) and di-isooctyl) adipate	13
47	Dioctylpentadeca dicarboxylate	19
48	Dimethylsilicone polymer (M.W. 3,000)	3
49	Mineral Oil SAE 30	22
50	Petroleum wax	4
51	Kendall base oil (SAE 10)	17
52	do	9
53	Kendall base oil (SAE 20)	
54	Cotton seed oil	2
55	Bis(2-ethylhexyl)sebacate	4
56	Kendall base oil (SAE 10)	23
57	Bis(2-ethylhexyl)adipate	26
58	Decyl decanoate	17.5
59	Naphthalene	11.5
60	Soybean oil	12.7
61	Paraffin	2.3

What is claimed is:

1. A lubricant composition comprising fatty acid diester of tripropylene glycol wherein each fatty acid moiety contains from about 6 to about 10 carbon atoms and from about 0.001% to about 5% of an antioxidant which is a mixture of p,p' - dioctyldiphenylamine and N-phenyl-1,2,3,4-tetrahydro-2-naphthylamine.

2. The composition of claim **2** wherein the ratio of p,p' - dioctyldiphenylamine and N - phenyl - 1,2,3,4-tetrahydro-2-naphthylamine is about 2:3.

3. The composition of claim **2** wherein the mixture of amine is present at 1.5% by weight of the lubricant composition.

4. The composition of claim **1** wherein 4% of said fatty acid moieties contain 6 carbon atoms, 55% of said fatty acid moieties contain 8 carbon atoms, about 40% of said fatty acid moieties contain 10 carbon atoms and about 1% of said fatty acid moieties contain 12 carbon atoms.

5. The composition of claim **1** wherein said fatty acid diester is tripropylene glycol dipelargonate.

6. The composition of claim **1** wherein said fatty acid diester is tripropylene glycol dicaprylate.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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Inventor(s) Robert Earl Wann

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Column 6, lines 30-31, delete "4% C_2, 55% C_8, 40% C_{10} and 1% C_{12}" and insert therefor --- C_6-4%; C_8-55%; C_{10}-40%; and C_{12}-1% ---

Column 8, line 18, after "claim" and before "wherein" delete "2" and Insert "1".

Signed and sealed this 9th day of January 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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