

## UNITED STATES PATENT OFFICE

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## CASTOR OIL LUBRICATING COMPOSITION

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10 Claims. (Cl. 252—33.4)

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This invention consists in improvements in the treatment of castor oil and related materials particularly to inhibit oxidation and/or "drying," gumming or hardening of such materials.

It is well known that castor oil, while possessing excellent lubricating properties, possesses the serious disadvantages of being prone to fairly rapid oxidation by atmospheric oxygen, leading to what is known as "drying," namely the hardening of the oil to form a solid resinous product or a sticky gum.

The rate of oxidation of fatty oils depends on the types of fatty acids present and particularly on their degree of unsaturation. The principal constituents of castor oil are the glycerides of ricinoleic acid, a hydroxy-substituted unsaturated fatty acid containing one ethylenic linkage. The oxidation which takes place is almost certainly accompanied by a polymerisation process in which the unsaturated molecules take part. The rate of oxidation and gum formation will, of course, depend on the temperature to which the oil is subjected and the presence of oxidation catalysts.

The invention relates not only to castor oil but to related materials such as the esters of ricinoleic acid, e. g., the simple esters of monohydric alcohols and the polyhydric alcohol esters, to lubricants consisting of mixtures of castor oil and mineral oil (comprising a major proportion of castor oil) and to the so-called castor-base greases containing a major proportion of castor oil.

It is one particular object of this invention to provide lubricating compositions suitable for use in internal combustion engines and for the lubrication of bearings, gears, etc. in which castor oil is the major ingredient. It is known to employ castor oil or mixtures of castor oil with minor amounts of mineral oil as lubricants in a variety of applications and especially in the lubrication of motor car and motor cycle engines where high speeds and severe operating conditions obtain. The excellent lubricating properties and high load-carrying capacity of

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such lubricants are well known, but they suffer from the serious disadvantage of gum formation due to oxidation and polymerisation. Furthermore the free acid normally present to some extent in castor oil and the acidic products produced on oxidation are liable to cause corrosion of composite metal (e. g. copper-lead) bearings under operating conditions.

It is accordingly an object of this invention to provide lubricants consisting of castor oil or mixtures of castor oil and mineral oil in which the castor oil is present in a major proportion, which lubricants have substantially increased resistance to oxidation and gum-formation under operating conditions and which are also relatively non-corrosive to composite metal bearings.

Other practical uses of this invention will be obvious to those who are familiar with the industrial uses of castor oil. Thus castor oil and blends of castor and mineral oil are used extensively for the lubrication of automotive and industrial gears. In such instances the question of corrosion does not arise, but resistance to gum formation is of great importance.

It is already known to inhibit the oxidation of fatty oils by the addition of various organic compounds of which the phenols (especially the polyhydric phenols) and the aromatic amines are examples.

Such compounds, however, suffer from the disadvantage that their effect is only of comparatively short duration.

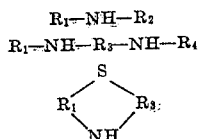
We have found that very much more effective resistance to oxidation and gum-formation can be obtained in the case of castor oil by the addition of a mixture of (a) an organic compound of tin or antimony and (b) an aromatic or heterocyclic secondary mono- or poly-amine containing at least three cyclic nuclei, at least two of which nuclei are aromatic nuclei attached directly to the nitrogen atom.

This invention in its broadest aspect therefore consists of a method of treating an oil of the kind described to inhibit oxidation and gumming which method consists in adding to the oil

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(a) a very small proportion of an organic compound of tin or antimony and (b) a very small proportion of an aromatic or heterocyclic secondary mono- or poly-amine containing at least three cyclic nuclei at least two of which nuclei are aromatic nuclei attached directly to the nitrogen atom.

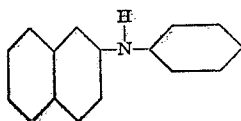
Typical formulae representative of the types of amines suitable for use in accordance with the present invention are:



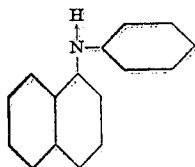
where  $R_1$ ,  $R_3$  and  $R_4$  are the same or different and are aromatic radicals, and  $R_2$  is a condensed aromatic nucleus having at least ten carbon atoms. Any or all of these radicals may be further substituted by alkyl, aryl, hydroxyl or amine groups, although the preferred substituents are hydrocarbon radicals only.

Specific examples of amines which may be employed are:

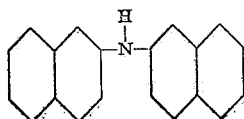
Phenyl- $\beta$ -naphthylamine



Phenyl- $\alpha$ -naphthylamine

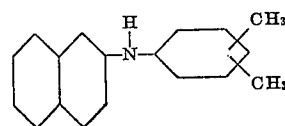


$\beta\beta$ -Dinaphthylamine

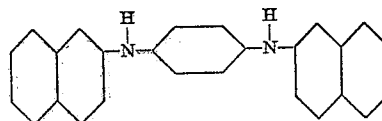


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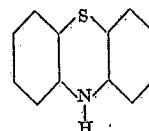
Xylol- $\beta$ -naphthylamine



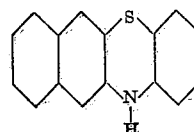
Di( $\beta$ -naphthyl)-p-phenylene diamine.



Phenothiazine



Thio-phenyl- $\beta$ -naphthylamine (benzonaphthothiazine)



We have found surprisingly that only amines of the type described are effective for the purpose of the present invention, such closely related amines as  $\alpha$ - and  $\beta$ -naphthylamine and diphenylamine being virtually without antioxidant effect.

The organic compounds of tin or antimony to be employed in conjunction with the amines already described are derivatives of divalent (stannous) tin or of antimony and may be the tin or antimony salts or soaps of organic carboxylic acids, organic sulphonic acids, organic dithiophosphoric acids, or the tin or antimony derivatives of phenols, phenol thioethers, or mercaptans. In the present specification and claims all of such compounds including the derivatives of phenols, phenol thioethers and mercaptans are considered to be salts of organic acidic compounds capable of salt formation.

Specific examples of appropriate organic compounds of tin are:

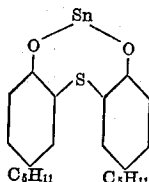
Tin laurate

Tin oleate

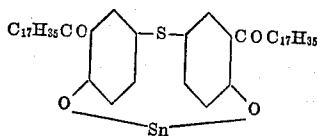
Tin naphthenate

Tin petroleum sulphonate

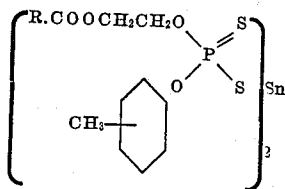
Tin derivative of p-tertiary amyl phenol thioether



Tin derivative of o-stearyl phenol thioether



Tin salt of ethylene glycol mononaphthenate cresyl dithiophosphate



where R.COOH=naphthenic acid.

It will be understood that the compounds selected must be soluble in the particular oil in the proportion in which they are to be employed.

We have found that whereas the tin compounds do not themselves possess any appreciable antioxidant or gum-inhibiting properties, they cooperate with the aromatic amines of the type described to give inhibition of oxidation over a period of time considerably longer than could be obtained by the use of the amines themselves in comparable proportions. In this respect the petroleum sulphonates of tin and antimony are particularly effective.

The aromatic amines used in this invention may be employed in amounts ranging from about 0.1 to about 5.0 per cent and preferably between 0.5 and 2.0 per cent depending on the particular material to be inhibited, and the conditions under which it is to be employed while the tin or antimony compounds may be employed in amounts

varying between about 0.05 and 2.0 per cent and preferably between 0.1 and 1.0 per cent. In general the best results are obtained when the amount of tin or antimony compound present does not exceed the amount of amine by weight and preferably the amount of amine employed is at least double the amount of tin or antimony compound.

In certain applications, notably the lubrication of internal combustion engines fitted with composite metal (e. g. copper-lead) bearings, the inhibition of the corrosion of said bearings at elevated temperatures becomes of importance.

We have found that whereas the combinations of additives already described possess excellent anti-oxidant properties they are not effective in retarding bearing corrosion appreciably.

By the addition of a third additive (c), however, not in itself effective to any great extent in reducing such corrosion produced by fatty acids and acidic oxidation products of castor oil, we have found surprisingly that a very substantial reduction in corrosion can be effected.

The additives falling within class (c) which may be employed where necessary in conjunction with the additives of classes (a) and (b) comprise the neutral organic phosphite esters of hydroxy-substituted aromatic thioethers and disulfides.

Specific examples of such phosphite esters are di-(3-carbomethoxy-4-hydroxy phenyl) thioether cresyl phosphite, and the phosphite ester of t-butyl cresol thioether. These materials may be employed in amounts ranging from about 0.2 to about 5.0 per cent and preferably from 0.5 to 2.0 percent.

If desired, further additives may be present in the compositions of this invention. Thus it may be desirable in certain instances to add viscosity index improvers, foam inhibitors, detergents, or ferrous metal corrosion inhibitors.

In particular we have found that certain additional benefits may accrue from the use in conjunction with the three types of additives already described of the reaction products of aldehydes or ketones with basic water-soluble primary or secondary amines.

We have found, for example that the addition of di-morpholinyl phenyl methane to a castor oil-mineral blend containing additives of types (a), (b) and (c) improved both its resistance to oxidation and its anti-corrosive properties. Advantage may accrue from the employment in certain instances of an antioxidant additive effective at high temperatures, along with the additives of the present invention. Such an antioxidant might be, for example, the metal salt of an organic dithiophosphoric acid or the metal derivative of an alkylated phenol thioether.

Lubricating oil compositions typical of those falling within the scope of the present invention are:

- (1) Firsts castor oil
  - +0.5% phenyl- $\beta$ -naphthylamine
  - +0.2% tin petroleum sulphonate
- (2) 90% acidless castor oil
  - 10% mineral lubricating oil of viscosity 500'' Redwood at 140° F.
  - +1.0% phenyl- $\beta$ -naphthylamine
  - +0.2% tin petroleum sulphonate

- (3) 87.5% firsts castor oil  
 12.5% mineral lubricating oil of viscosity 44"  
 Redwood at 140° F.  
 + 1.0% phenyl- $\beta$ -naphthylamine  
 0.2% tin petroleum sulphonate  
 2.0% di (3-carbomethoxy-4-hydroxyphenyl) thioether cresyl phosphite  
 0.2% dimorpholinyl phenyl methane

By "tin petroleum sulphonate" is meant the tin salt of the oil-soluble petroleum sulphonic acids commonly known as "mahogany acids."

The following series of tests were carried out to determine the effectiveness of the compounds of the present invention:

#### A. GUMMING TESTS AT 120° C.

One drop of the oil was placed in the centre of a watch-glass and heated at 120° C. in an oven for a prolonged period. At intervals the watch glasses were withdrawn, allowed to cool and the liquid examined for signs of tackiness or gum formation.

The majority of the test results quoted were the mean of two or more such tests.

Table 1.—Tests in this table serve to illustrate the surprising advantage of the use of the combination of two additives of the present invention over that of either additive used separately.

A blend of:

- 90% acidless castor oil  
 10% mineral lubricating oil of viscosity 500"  
 Redwood at 140° F. (Oil A)

was used as a basis for experimentation.

Table 1

Test No.	Additives		Approximate time (hours) to—	
	Amine	Tin or antimony compound	Incidence of tackiness	Gum formation
1	None	None	18	33
2	do	Tin petroleum sulphonate (0.2%).	18	23
3	Phenyl- $\beta$ -naphthylamine (1%).	None	110	125
4	Phenyl- $\beta$ -naphthylamine (0.5%).	do	80	90
5	Phenyl- $\beta$ -naphthylamine (1%).	Tin petroleum sulphonate (0.2%).	320	440
6	Phenyl- $\beta$ -naphthylamine (0.5%).	Tin petroleum sulphonate (0.2%).	157	190
7	Phenyl- $\beta$ -naphthylamine (1.0%).	Tin petroleum sulphonate (1.0%).	156	200
8	Phenyl- $\beta$ -naphthylamine (0.5%).	Antimony petroleum sulphonate (0.2%).	160	180
9	Phenyl- $\alpha$ -naphthylamine (1.0%).	None	115	135
10	Phenyl- $\alpha$ -naphthylamine (1.0%).	Tin petroleum sulphonate (0.2%).	160	185

Table 2.—Tests in this table illustrate the range of tin and antimony compounds which may be employed in conjunction with a typical amine.

- A blend of (90% acidless castor oil and 10% mineral lubricating oil of viscosity 500" Redwood at 140° F.—Oil A) + phenyl- $\beta$ -naphthylamine (PBN) was employed throughout.

Table 2

Test No.	Amount of PBN present, percent	Metal compound added	Approximate time (hours) to—	
			Incidence of tackiness	Gum formation
1	1.0	None	100	125
2	1.0	Tin petroleum sulphonate (0.2%)	320	440
3	1.0	Tin naphthenate (0.2%)	170	185
4	1.0	Tin oleate (0.2%)	125	145
5	1.0	Tin derivative of p-tertiary amyl phenol thioether (0.2%).	165	180
6	0.5	None	80	90
7	0.5	Tin petroleum sulphonate (0.2%)	157	190
8	0.5	Tin laurate (0.2%)	120	130
9	0.5	Tin derivative of o-stearyl phenol thioether (0.2%).	130	155
10	0.5	Tin salt of ethylene glycol mononaphthenate cresyl di-thiophosphate (0.2%).	115	125
11	0.5	Antimony petroleum sulphonate (0.2%).	160	180
12	0.5	Antimony naphthenate (0.2%)	120	135

While, therefore, benefit accrued from the use of a wide variety of tin and antimony compounds, the petroleum sulphonates were outstandingly effective.

- Table 3.—Tests in this table illustrate the types of amines which may be employed in carrying out the present invention, in addition to those already cited in Table 1. The same blend was used as before.

Table 3

Test No.	Amine	Tin petroleum sulphonate present, percent	Approximate time (hours) to—	
			Incidence of tackiness	Gum formation
1	$\beta\beta$ -Dinaphthylamine (0.5%).	0.2	180	200
2	Xylyl- $\beta$ -naphthylamine (0.5%).	0.2	145	160
3	Phenothiazine (0.5%).	0.2	205	220
4	Benzonaphthothiazine	0.2	205	225
5	Diphenylbenzidine (saturated solution, less than 0.5%).	0.2	Over 320	
6	Di- $\beta$ -naphthyl-p-phenylene diamine (0.5%).	0.2	320	345
7	$\beta$ -Naphthylamine (0.5%).	0.2	Less than 60	85
8	Diphenylamine (0.5%).	0.2	40	65
9	Triphenylamine (1.0%).	0.2	18	28

The last three results are quoted for comparative purposes to illustrate the relative ineffectiveness of certain amines closely related to those of the present invention.

- Table 4.—Tests in this table illustrate the range of ricinoleic acid derivatives which may be inhibited against gum formation by the additives of the present invention, and also the use of supplementary additives.

Table 4

Test No.	Material inhibited	Inhibitors added	Approximate time (hours) to—	
			Incidence of tackiness	Gum formation
1	Firsts castor oil	None		
2	do	1% Phenyl- $\beta$ -naphthylamine 0.2% Tin petroleum sulphonate 2.0% Di(3-carbomethoxy-4-hydroxy-phenyl)thioether cresyl phosphite 0.2% Dimorpholinyl phenyl methane	21	28
3	90% acidless castor oil 10% mineral oil A	None	400	440
4	90% acidless castor oil 10% mineral oil A	1% phenyl- $\beta$ -naphthylamine 0.2% tin petroleum sulphonate 2% di(3-carbomethoxy-4-hydroxyphenyl) cresyl phosphite	18	33
5	90% acidless castor oil 10% mineral oil A	As No. 4 with the addition of 0.2% dimorpholinyl phenyl methane	230	250
6	Butyl ricinoleate	None	250	275
7	do	1% phenyl- $\beta$ -naphthylamine	54	
8	do	As No. 7 with the addition of 0.2% tin petroleum sulphonate	235	285
9	Glyceryl diricinoleate	None	255	
10	do	1% phenyl- $\alpha$ -naphthylamine 0.2% tin petroleum sulphonate	20	40
			120	175

## B. CORROSION TESTS

The following test was employed for obtaining information as to the tendency for corrosion of composite metal bearings, particularly copper-lead bearings, to occur in use of lubricating compositions provided by the present invention.

400 ml. of lubricant was weighed into 1500 ml. tall lipless glass beakers, eight of which were heated in a circular electrically heated oil bath thermostatically controlled to maintain the lubricant temperature at 140° C. The beakers were equipped with closely fitted aluminium covers having central slides which were normally closed but capable of being opened for the insertion of a test specimen. The slides when closed allowed sufficient clearance for centrally placed steel stirring rods to revolve freely. The latter were electrically driven from a common driving shaft at 400±40 R. P. M. and carried at their lower end

Tests were conducted for 12 hours in two periods of six hours, the copper and lead specimens being removed every two hours and replaced by fresh clean ones. Copper catalysts were cleaned with carborundum powder and washed in petroleum ether. Lead specimens were flattened, scraped with a special scraper and finally polished by brushing in one direction with file carding before washing in benzene and weighing. After a 2 hour period a further washing in benzene, brushing with a camel hair brush and reweighing was effected. The total corrosion was calculated by adding together the weight losses of the lead specimens after each two-hour period.

The following test results illustrate the effectiveness of the hydroxyaryl thioether phosphites in conjunction with the other additives of the present invention, in inhibiting corrosion of lead at elevated temperatures.

Table 5

Test No.	Oil	Additives	Lead specimen weight loss (cumulative) after—			
			2 hours	4 hours	6 hours	12 hours
1	90% acidless castor oil 10% mineral oil A	None				
2	90% acidless castor oil 10% mineral oil A	0.5% phenyl- $\beta$ -naphthylamine 0.3% tin petroleum sulphonate 1.0% phenyl- $\beta$ -naphthylamine 0.2% tin petroleum sulphonate 2.0% di(3-carbomethoxy-4-hydroxy-phenyl) thioether cresyl phosphite 0.2% dimorpholinyl phenyl methane	58	153		
3	90% acidless castor oil 10% mineral oil A	1.0% phenyl- $\beta$ -naphthylamine 0.2% tin petroleum sulphonate 2.0% di(3-carbomethoxy-4-hydroxy-phenyl) thioether cresyl phosphite 0.2% dimorpholinyl phenyl methane	264	371		
4	90% acidless castor oil 10% mineral oil A	1.0% phenyl- $\beta$ -naphthylamine 0.2% tin petroleum sulphonate 2.0% tertiary butyl cresyl thioether phosphite 1.0% phenyl- $\beta$ -naphthylamine 0.2% tin petroleum sulphonate	4	37	81	204
5	90% acidless castor oil 10% mineral oil A	1.0% phenyl- $\beta$ -naphthylamine 0.2% tin petroleum sulphonate 1.0% di(3-carbomethoxy-4-hydroxy-phenyl)thioether cresyl phosphite 1.0% zinc di( $\alpha$ -methyl isoamyl) dithiophosphate	6	102	263	
			13	25	42	135

## C. ENGINE TESTS

Tests were carried out in a standard H-2 type Lauson engine under the following conditions:

Jacket temperature ..... 210°±2° F.  
Oil sump temperature ..... 280°±2° F.  
Test duration ..... 60 hours.

The following test results illustrate the effectiveness of certain of the compositions contemplated in the present invention as lubricants for

slotted holders to which lead test pieces were attached by means of screws. For the test-pieces rectangular plates of pure lead 1¾" by 1" were mounted vertically just below the surface of the lubricant with the longer axis horizontal. Copper strips, as catalysts, ½" wide and bent into a semi-circle 3¾" in diameter were placed wholly below the surface of the lubricant and attached by means of vertical copper wires to corks fitted in the beaker covers. Each beaker was also fitted with a thermometer.

internal combustion engines operating under severe conditions:

Table 6

Test No.	Lubricant	Piston lacquer rating (C. R. C. visual rating)	Bearing weight loss, mgs.	Used oil analysis	
				Percent visc. inc.	Acidity (mgs. KOH per gm.)
1	87.5% acidless castor oil 12.5% mineral oil B (No. 1-1% phenyl-β-naphthylamine), 0.2% tin petroleum sulphamate).	8.7	513	285	5.2
2	2% di(3-carbomethoxy-4-hydroxyphenyl)thioether cresyl phosphite, 0.2% dimorpholinyl phenyl methane.	8.2	68 (Mean figures—2 tests)	156	5.0
3	87.5% firsts castor oil 12.5% mineral oil B	8.5	509	442	5.9
4	No. 3+the same additives employed in test No. 2.	8.3	103 (Mean figures—2 tests)	175	6.5

In tests 1 and 3 there was a very heavy build-up of soft black gum on the neck of the inlet valve. In tests 2 and 4 the amount of deposit on the inlet valve was extremely light.

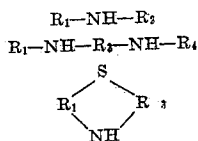
Oil B was a mineral lubricating oil of viscosity 44" Redwood at 140° F.

The method of rating piston cleanliness was that adopted by the Co-ordinating Research Council (C. R. C.) in which a perfectly clean piston is given a rating of 10 and a perfectly black piston a rating of zero.

We claim:

1. A lubricating composition comprising a major proportion of castor oil in which is incorporated a proportion of from 0.05% to 2.0% of a metallic organic compound soluble in castor oil and selected from the group consisting of tin and antimony salts of aliphatic monocarboxylic acids having 12 to 18 carbon atoms, organic sulphonc acids, naphthenic acids, and phenol thioethers and a proportion of from 0.1% to 5.0% of an aromatic secondary amine containing at least three cyclic nuclei, at least two of which nuclei are aromatic nuclei attached directly to the nitrogen atom.

2. A lubricating composition as claimed in claim 1 in which the amine is selected from the group consisting of a compound represented by the general formula



where  $R_1$ ,  $R_3$  and  $R_4$  are aromatic radicals and  $R_2$  is a condensed aromatic nucleus having at least ten carbon atoms.

3. A lubricating composition as claimed in claim 1 in which is incorporated a proportion of from 0.2% to 5.0% of a neutral organic phosphite ester of a hydroxy-substituted aromatic thioether.

4. A lubricating composition as claimed in claim 1 in which is incorporated a proportion of from 0.2% to 5.0% of a neutral organic phosphite ester of a hydroxy-substituted aromatic disulfide.

5. A lubricating composition as claimed in claim 1 comprising also a minor proportion of a further lubricant additive selected from the group consisting of the reaction product of an aldehyde with a basic water-soluble amine and the reaction product of a ketone with a basic water-soluble amine.

6. A lubricating composition as claimed in claim 1, comprising also a proportion of up to 12½% of a mineral oil.

7. A lubricating composition comprising a major proportion of castor oil in which is incorporated a proportion of from 0.05% to 2.0% of a castor oil soluble tin salt of an organic sulphonc acid and a proportion of from 0.1% to 5.0% of an aromatic secondary amine containing at least three cyclic nuclei, at least two of which nuclei are aromatic nuclei attached directly to the nitrogen atom.

8. A lubricating composition comprising a major proportion of castor oil in which is incorporated a proportion of from 0.05% to 2.0% of a castor oil soluble antimony salt of an organic sulphonc acid and a proportion of from 0.1% to 5.0% of an aromatic secondary amine containing at least three cyclic nuclei, at least two of which nuclei are aromatic nuclei attached directly to the nitrogen atom.

9. A lubricating composition comprising a major proportion of castor oil in which is incorporated a proportion of from 0.05% to 2.0% of tin petroleum sulphamate and a proportion of from 0.1% to 5.0% of an aromatic secondary amine containing at least three cyclic nuclei, at least two of which nuclei are aromatic nuclei attached directly to the nitrogen atom.

10. A lubricating composition comprising a major proportion of castor oil in which is incorporated a proportion of from 0.05% to 2.0% of antimony petroleum sulphamate and a proportion of from 0.1% to 5.0% of an aromatic secondary amine containing at least three cyclic nuclei, at least two of which nuclei are aromatic nuclei attached directly to the nitrogen atom.

#### References Cited in the file of this patent

#### UNITED STATES PATENTS

Number	Name	Date
55 1,163,856	Rice	Dec. 14, 1915
1,594,983	Sommervill	Aug. 3, 1926
2,410,652	Griffin et al.	Nov. 5, 1946
2,440,530	Yates	Apr. 27, 1948
2,472,503	Minne	June 7, 1949
60 2,551,124	Helmore	May 1, 1951
2,579,038	Evans et al.	Dec. 18, 1951

#### FOREIGN PATENTS

Number	Country	Date
65 616,881	Great Britain	Jan. 28, 1949