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RESINOUS ESTER

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This invention relates to mixed resinous esters, and more particularly to such esters wherein the alcohol is either pentaerythritol or a polypentaerythritol such as dipentaerythritol, and wherein the alcohol is esterified with a rosin acid and with a fatty acid derived from a drying oil or a semi-drying oil.

Mixed glycerine esters of rosin and the fatty acids derived from drying oils have been heretofore known to the art, but films of these esters are slow drying and display very poor alkali and water resistance. It has also been proposed in U. S. 1,667,189 to prepare a synthetic resin by esterifying pentaerythritol with the dibasic acid phthalic anhydride and with a drying oil fatty acid such as linseed oil fatty acid together with rosin, the fatty acid and the rosin on a molar basis amounting to sufficient to occupy only 1.3 of the 4 hydroxyl groups presented by the pentaerythritol. The resins prepared in that manner are of the type which become insoluble and infusible upon baking.

It is an object of the present invention to provide a synthetic resin exhibiting properties superior to those of the prior art resins discussed above.

Another object is to provide a method for the preparation of such esters.

Still other objects will more fully hereinafter appear.

In accordance with the present invention, the foregoing objects are accomplished in general by esterifying pentaerythritol or a polypentaerythritol such as dipentaerythritol with a rosin acid in amount sufficient to occupy from about 10% to about 75% of the hydroxyl groups presented by the alcohol employed and with a fatty acid having an unsaturation at least equal to that of the fatty acids contained in the semi-drying oils and preferably that of the fatty acids contained in drying oils, the fatty acid being used in an amount sufficient to occupy from about 25% to about 90% of the hydroxyl groups presented by the alcohol employed. Preferably, the rosin acid and the fatty acid are the sole acid components combined with the alcohol in the condensation product.

The resinous mixed ester or condensation product produced by esterifying pentaerythritol or dipentaerythritol with the foregoing proportions of rosin acid and unsaturated fatty acid of the type found in drying oils and semi-drying oils exhibits properties far superior to those of the corresponding esters prepared with glycerine especially when used in conjunction with soft drying oils such as linseed oil, dehydrated castor oil and the like. The esters of the present invention display improved drying characteristics in the resulting varnish and increase the hardness, alkali resistance, and water resistance of the resulting varnish film.

As the rosin acid, I may use any type of rosin such as wood rosin or gum rosin, or equivalent acids such as abietic acid, or I may use a modified rosin such as heat-treated rosin, disproportionated rosin, hydrogenated rosin, polymerized rosin, etc. Preferably, the rosin acid employed is one which has been previously refined to at least an N grade on the scale of U. S. standard rosin types.

As the fatty acid, I may use any fatty acid derived from drying or semi-drying oils, or equivalent unsaturated monobasic acids prepared synthetically or otherwise. Typical examples are fatty acids derived from linseed oil, soybean oil, dehydrated castor oil, poppyseed oil, tung oil, sunflower oil, corn oil, cotton-seed oil, sesame oil, sardine oil, menhaden oil, etc.

As the polyhydric alcohol, I may employ pentaerythritol, or a polypentaerythritol, preferably dipentaerythritol, or mixtures of pentaerythritol and dipentaerythritol such as, for example, the crude mixture thereof directly obtained by certain processes of condensing acetaldehyde with formaldehyde and containing up to about 25% by weight of dipentaerythritol. Instead of dipentaerythritol, higher polypentaerythritols may be used such as for example tripentaerythritol, etc.

The condensation product prepared with pentaerythritol preferably contains combined rosin acid in amount sufficient to occupy from about 1 to about 2.0 of the 4 hydroxyl groups presented by the pentaerythritol and with the fatty acid in amount sufficient to occupy from about 2.0 to about 3.0 of the 4 hydroxyl groups presented by the pentaerythritol, the rosin acid and the fatty acid together occupying at least about 3.6 of the 4 hydroxyl groups of the pentaerythritol. The combined acid components may vary from about 3.6 upwardly to 4.0 mols per mol of pentaerythritol.

When using dipentaerythritol, preferably rosin acid is employed in an amount sufficient to occupy from about 1.5 to about 3.0 of the 6 hydroxyl groups presented by the dipentaerythritol and the fatty acid in amount sufficient to occupy from about 3.0 to about 4.5 of the hydroxyl groups of the dipentaerythritol, the combined rosin acid and fatty acid together occupying from about 5.5 upwardly of the 6 hydroxyl groups of the dipentaerythritol.

If desired, an excess of the polyhydric alcohol

may be employed, ranging upwardly to a 20% excess over the theoretical for the amounts of rosin acid and fatty acid taken. Preferably, this excess should not exceed the figure of 20% in order that the water resistance of the resulting resinous ester may be satisfactory.

Preferably, the components of the resin are so proportioned and reacted that the product has an acid number of not over about 25.

The physical state of the resulting resin will depend upon the proportions employed. The resin will be liquid when the proportion of fatty acid employed is relatively high, will be a plastic-type material when the content of fatty acid ester is from about 40% to about 70% of the product considered as a mixture of the fatty acid ester and the rosin acid ester, and will be a solid when the content of fatty acid ester is from about 20% to about 40%.

The resinous materials of the present invention may be extended with additional quantities of drying oils added during the preparation or may subsequently be cooked with drying oils such as tung oil, soft drying oils like linseed oil, dehydrated castor oil, soybean oil, etc., to form varnishes displaying superior characteristics.

Any of the resinous materials of the present invention may be cut or diluted with a suitable thinner, suitable amounts of suitable driers added, and the resulting mixture used as a coating composition. If the resin is to be applied as a film it generally will be preferable to employ such as solvent. However, by certain specific procedures, such as spraying the hot resin, or hot melt application by roller coating equipment, the resin can be applied without this solvent addition. The liquid resinous esters of the present invention may be used directly, upon the proper addition of driers, as a coating composition.

When the resin contains a relatively small proportion of fatty acid ester of pentaerythritol or polypentaerythritol, it may be transferred to another vessel and cooked with additional oil to prepare a varnish. For most purposes, however, it is desirable that any additional oil be added to the resin during its preparation, and the resulting material dissolved in a suitable solvent, driers added, and the product used as a varnish.

Suitable driers may be incorporated in the resins of the present invention to improve drying speed and hardness of film. The amount and type of drier employed will be within the skill of the art.

The resin may be prepared by several methods, among which are the following.

1. The fatty acid and polyhydric alcohol are first esterified to a low acid number, below 25, at temperatures ranging from 175° C. to 300° C., the optimum temperature being from 225° C. to 250° C., the rosin acid is then added and the esterification again carried to a low acid number at a temperature ranging from 250° C. to 310° C., the optimum being 285° C., and the temperature then being finally raised to between 300° C. and 350° C., the optimum being from 305° C. to 315° C., and held at this final temperature until a cooled sample will form a gelled pill. The finished resin may then be reduced to 50% solids with mineral spirits.

2. The rosin acid and the polyhydric alcohol are first esterified at 285° C. to 295° C. to a low acid number, the fatty acid then added and the esterification carried out at 200° C. to 250° C. to a low acid number, the resin being finally heated if desired to a temperature of from 300° C. to 350° C., the optimum being from 305° C. to 315° C., until a cooled sample forms a gelled pill. This resin may then be reduced to 50% solids with mineral spirits.

3. The rosin acid, fatty acid and the pentaerythritol or dipentaerythritol are esterified at 285° C. to 290° C. to a low acid number, the resin then being heated to between 300° C. and 350° C., the optimum being 305° C. to 315° C., until the cooled sample forms a gelled pill. This resin may then be reduced to 50% solids with mineral spirits as before.

If desired, the fatty acid may be introduced to the reaction mixture in the form of its ester, relying upon alcoholysis to cause the desired reaction. For example, the methyl ester of soya bean fatty acid may be employed instead of soya bean fatty acid itself as a component of the reaction mixture. Upon heating to say between 180° C. and 235° C. in the normal reaction procedure, alcoholysis takes place and the methyl alcohol volatilizes. By this procedure acid numbers are reduced to 5 or under in a relatively few hours, whereas it is extremely difficult to bring acid numbers much under 20 during the course of several hours by means of direct esterification using soya bean fatty acid itself as the fatty acid may be added in the form of its tri-, di-, or monoglyceride, relying upon ester interchange.

Following are illustrative examples of preferred embodiments of the present invention.

Example 1

	Parts by weight	Relative molar amts.
N wood rosin (assumed molecular weight, 340)	300	1.11
Pentaerythritol	108	1.0
Linseed oil fatty acids (assumed average mol. wt., 285)	600	2.66

The rosin was heated to 100° C. whereupon the pentaerythritol was added. The mixture was heated to a temperature of 285–295° C., and held there until the acid number had dropped below 10. This required 6 hours. The linseed oil fatty acid was then added to the mixture causing the temperature to drop below 150° C. The mixture was then heated to 250° C. for 3 hours. The temperature was then slowly raised over a period of 3½ hours to 290° C. and held there for 3½ hours at which point the acid number had dropped below 20. The temperature was then raised to 307° C. and held there for 3½ hours at which time a sample of the ester when cooled on a tin plate formed a gelled pill. Carbon dioxide was slowly bubbled through the reaction vessel and mixture throughout the esterification. The resulting ester was reduced to 50% solids with mineral spirits. The ester had an acid number of 11.2, a color of 3L (Hellige) and the solution had a viscosity of C–D on the Gardner-Holdt scale.

Example 2

	Parts by weight	Relative molar amts.
Polymerized rosin (drop M. P. about 100° C., assumed mol. wt. 360)	300	1.05
Pentaerythritol	108	1.0
Linseed oil fatty acid as in Example 1	600	2.66

The polymerized rosin was heated to 100° C. whereupon the pentaerythritol was added, the

mixture heated to a temperature of 285–295° C. and held there until the acid number had dropped below 10 which required 6 hours. The linseed oil fatty acid was then added causing the temperature to drop below 150° C. The mixture was then heated to 250° C. and held there for 3 hours. The temperature was then slowly raised over a period of 3½ hours to 290° C. and held at that temperature for 3½ hours at which point the acid number had dropped to 18.

Example 3

	Parts by weight	Relative molar amts.
N wood rosin (as in Example 1)	300	1.11
Pentaerythritol	108	1.0
Soybean oil fatty acid (average mol. wt. 283)	600	2.67

The rosin was heated to 100° C. and the pentaerythritol added. The mixture was raised to 285° C.–295° C. and held there until the acid number had dropped below 10 which required 6 hours. The soy-bean oil fatty acid was then added causing the temperature to drop below 150° C. The mixture was heated to 250° C. and held there for 3 hours. The temperature was then slowly raised over a period of 3½ hours to 290° C. and held there for 3½ hours at which point the acid number had dropped to 14. The temperature was then raised to 307° C. and held there for 5¼ hours. The ester had an acid number of 7.1, a color of 2L–2, and was reduced to 50% solids with mineral spirits to give a solution having a viscosity of less than A on the Gardner-Holdt scale.

Example 4

	Parts by weight	Relative molar amts.
N wood rosin (as in Example 1)	300	1.8
Dipentaerythritol	123	1.0
Linseed oil fatty acid (as in Example 1)	600	4.3

The rosin was heated to 100° C. and the dipentaerythritol introduced, the mixture heated to 285–295° C. and held there until the acid number had dropped below 10 which required 6 hours. The linseed fatty acid was then added, causing the temperature to drop below 150° C. The temperature was raised to 250° C. and held there for 3 hours. The temperature was then slowly raised over a period of 3½ hours to 290° C. and held for 3½ hours at which point the acid number had dropped 24. The temperature was then raised to 307° C. and held there for 2¼ hours at which time a sample of the ester when cooled on a tin plate formed a gelled pill. This ester had an acid number of 12.1, a color of 2 and when reduced to 50% solids with mineral spirits formed a solution having a viscosity of J.

Example 5

	Parts by weight	Relative molar amts.
WW gum rosin (assumed mol. wt. 340)	192	1.45
Soybean oil fatty acids (as in Example 3)	255	2.31
Pentaerythritol	53	1.0

These ingredients were admixed and the mixture heated to 285° C. over a period of 3 hours and held there for ½ hour when the acid number was less than 13.7. The mixture was sparged during the last hour of this heating with carbon dioxide. The reaction product was cut to 50% solids with mineral spirits of the type known as "Varsol." The resulting solution had a viscosity of A— on the Gardner-Holdt scale and a color of 4 Hellige.

Example 6

	Parts by weight	Relative molar amts.
N wood rosin (as in Example 1)	88.5	3.0
Pentaerythritol	13.3	1.0
Linseed oil fatty acid (as in Example 1)	68	1.0

The rosin and pentaerythritol were admixed and heated to 285° C. for 8 hours. The resin obtained had an acid number of 13. The linseed oil fatty acid was added and the mixture heated at 200–225° C. for 7 hours. The resin had an acid number of 20 and was a semi-solid balsam-like material.

Example 7

The procedure of Example 6 was duplicated exactly except that dehydrated castor oil fatty acid was employed.

Example 8

The procedure of Example 6 was duplicated exactly except that soya bean fatty acid was substituted for the linseed oil fatty acid.

From the foregoing it will be seen that the present invention enables the ready production of an improved resin for use in the arts, particularly in the field of coating compositions. In its application the resinous product may be commingled with any other components commonly used in liquid coating compositions which are compatible therewith, such as other resins, plasticizers, driers, oils, pigments, dyes, and the like. The resinous product of the present invention is markedly superior to a corresponding resin made with glycerine and to a corresponding resin made without the fatty acid. Varnishes made therewith yield films of superior hardness, abrasion resistance, toughness, and resistance to water and alkali.

Since dibasic acids, such as for example phthalic anhydride, maleic anhydride, etc., are not used in the preparation of the resins of the present invention, difficulties due to that type of gelation to an insoluble infusible stage which occurs when a polybasic acid is used with a trihydric or higher polyhydric alcohol, are positively avoided. The acids which I use are all monobasic and these monobasic acids which I use, such as a rosin acid and a fatty acid, are cheaper than the dibasic acids which is an additional advantage. Moreover, the resinous esters of the present invention are in general more stable in regard to their viscosity characteristics on storage than are resins made with the dibasic acids.

It will be understood that the details and examples hereinbefore set forth are illustrative only and that the invention as broadly described and claimed is in no way limited thereby.

What I claim and desire to protect by Letters Patent is:

1. As a new article of manufacture, a condensation product of an alcohol selected from the group consisting of pentaerythritol and polypentaerythritols with polymerized rosin in amount sufficient to occupy from about 10 per cent to about 75 per cent of the hydroxyl groups presented by said alcohol and with a fatty acid

having an unsaturation within the range of the unsaturation of the fatty acids in the drying and semi-drying oils in an amount sufficient to occupy essentially entirely the remaining about 25 per cent to about 90 per cent of the hydroxyl groups presented by said alcohol.

2. As a new article of manufacture, a condensation product of an alcohol selected from the group consisting of pentaerythritol and polypentaerythritols with polymerized rosin in amounts sufficient to occupy from about 10% to about 75% of the hydroxyl groups presented by the said alcohol and with a fatty acid having an unsaturation within the range of the unsaturation of the fatty acids in the drying and semi-drying oils in an amount sufficient to occupy from about 25% to about 90% of the hydroxyl groups presented by the said alcohol, the acid groups of the condensation product consisting essentially of polymerized rosin acid groups and fatty acid groups.

3. As a new article of manufacture, a condensation product of pentaerythritol with acids consisting essentially of a polymerized rosin acid in amounts sufficient to occupy from about 1.0 to about 2.0 of the four hydroxyl groups of the pentaerythritol and a fatty acid having an unsaturation within the range of the unsaturation of the fatty acids in the drying and semi-drying oils in an amount sufficient to occupy from about 2.0 to about 3.0 of the four hydroxyl groups of the pentaerythritol, the said polymerized rosin acid and the said fatty acid occupying at least about 3.6 of the four hydroxyl groups of the pentaerythritol.

4. As a new article of manufacture, a condensation product of dipentaerythritol with a polymerized rosin acid in amounts sufficient to occupy from about 1.5 to about 3.0 of the six hydroxyl groups presented by the dipentaerythritol and with a fatty acid having an unsaturation within the range of the unsaturation of the fatty acids in the drying and semi-drying oils in amounts sufficient to occupy from about 3.0 to about 4.5 of the six hydroxyl groups presented by the dipentaerythritol, the said polymerized rosin and the said fatty acid occupying at least about 5.5 of the six hydroxyl groups of the dipentaerythritol, the acid groups of the product consisting essentially of the polymerized rosin and the fatty acid groups.

5. As a new article of manufacture, a condensation product of pentaerythritol with polymerized rosin in an amount sufficient to occupy from about 10% to about 75% of the hydroxyl groups of the pentaerythritol and with drying oil fatty acids in an amount sufficient to occupy from about 25% to about 90% of the hydroxyl groups of the pentaerythritol, the acid groups of the product consisting essentially of the polymerized rosin and the fatty acid groups.

6. As a new article of manufacture, a condensation product of pentaerythritol and acids consisting essentially of polymerized rosin acid in an amount sufficient to occupy from about 10% to about 75% of the hydroxyl groups of the pentaerythritol and linseed oil fatty acids in an amount sufficient to occupy from about 25% to about 90% of the hydroxyl groups of the pentaerythritol.

7. As a new article of manufacture, a condensation product of pentaerythritol and acids consisting essentially of polymerized rosin acid in an amount sufficient to occupy from about 10% to about 75% of the hydroxyl groups of the pentaerythritol and tung oil fatty acids in an amount sufficient to occupy from about 25% to about 90% of the hydroxyl groups of the pentaerythritol.

8. As a new article of manufacture, a condensation product of pentaerythritol and acids consisting essentially of polymerized rosin acid in an amount sufficient to occupy from about 10% to about 75% of the hydroxyl groups of the pentaerythritol and dehydrated castor oil fatty acids in an amount sufficient to occupy from about 25% to about 90% of the hydroxyl groups of the pentaerythritol.

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