Patented Nov. 4, 1952 2,616,865

UNITED STATES PATENT OFFICE

2,616,865

VINYL CHLORIDE AND VINYL ACETATE COPOLYMER PLASTICIZED WITH MIXED ESTERS OF TETRAHYDROFURFURYL ALCOHOL

Emery I. Valko, Mountain Lakes, N. J., assignor to E. F. Drew & Co., Inc., New York, N. Y., a corporation of Delaware

No Drawing. Application May 7, 1949, Serial No. 92,070

2 Claims. (Cl. 260—27)

1

The present invention is directed to plasticizers for use with various synthetic resins, more particularly to plasticizers of the ester type.

In recent years the use of esters of various acids, both monobasic and polybasic, has become quite common as plasticizing agents for various synthetic resins and similar plastic compositions. Among such plasticizers are the neutral polyglycol esters of mixtures of fatty acids having 8 and 10 carbon atoms. Such plasticizers have been quite satisfactory in most respects as they have had good compatibility with resinous materials such as the polyvinyl resins, and they have proven to be quite efficient. However, the raw materials are sometimes unavailable and sometimes high in cost. Care must be taken in the manufacture of the esters, so that close supervision is necessary. Similar considerations apply to esters of different types, such as those of the polybasic acids.

The present invention is intended and adapted to overcome the disadvantages inherent in prior plasticizers of the ester type, it being among the objects of the present invention to provide a new esterified composition which is adapted for various uses, and which may be manufactured from readily available raw materials at a low cost.

It is also among the objects of the present invention to provide a resinous composition plasticized with the new esters, which composition exhibits a high degree of compatibility of the plasticizer and a high efficiency in its effects.

It is further an object of the present invention to utilize as a raw material a mixture of rosin and higher fatty acids, which mixture may be naturally occurring or synthetic, and which fatty acids may be likewise natural or synthetic.

It is still further among the objects of the present invention to provide a method of making ester plasticizers from such mixture of rosin and free fatty acids, which is highly effective, is simple, and which results in a substantially complete esterification with the resulting product having a low acid number.

The invention is based upon the discovery that mixtures of esters of rosin with tetrahydrofurfuryl alcohol with esters of higher fatty acids and tetrahydrofurfuryl alcohol have a high efficiency and high compatibility when incorporated in resinous materials. It has also been discovered that these two types of esters are mutually soluble in a great variety of proportions to give the aforesaid high effectiveness.

Both the higher fatty acids and the rosin are relatively less reactive than the lower fatty acids

2

and the esterification thereof may be expected to present difficulties. Because the tetrahydrofurfuryl alcohol is readily volatile a limitation to a relatively low reaction temperature to form the esters is necessary. The combination of these two factors made it doubtful that the reaction to form the esters would go to substantial completion or even to give a partial esterification. However, in actual practice it was found that excellent results were obtained.

In practicing the present invention there is provided a mixture of rosin and fatty acids, the latter having at least 10 carbon atoms and usually up to 22 carbon atoms. To this is added a substantial amount of rosin and the proportions of rosin and mixed fatty acids may vary between 30% and 70% of rosin to 70% to 30% of the free fatty acids. Various proportions have been found suitable but a composition having approximately equal quantities by weight of rosin and the fatty acids have been found particularly effective in plasticizing a copolymer of vinyl chloride and vinyl acetate.

The reaction is carried on usually in several stages wherein the principal reaction is caused to take place in the first stage to cause a substantial amount of esterification. In the further stages, an additional quantity of the alcohol is added and the esterification continued until the acid number is quite low. It is perfectly feasible to obtain a product having an acid number of not over 10 and it is quite simple to reduce the acid number to below 5 in the usual second stage of the esterification. The acid number may be reduced still further by various means.

The following are specific examples of the operation of the invention.

EXAMPLE 1

A naturally occurring mixture of rosin and unsaturated higher fatty acids including a minor proportion of saturated fatty acids and some impurities, and known as tall oil, is the starting material. A tall oil containing about 33% of rosin is mixed in equimolecular proportions with tetrahydrofurfuryl alcohol, the amount of tall oil being 1240 grams and the amount of alcohol being about 410 grams. There is added a small amount, say .2% of lead oxide as a catalyst.

The mixture is heated for about 6 hours with a reflux condenser so as to return vaporized tetrahydrofurfuryl alcohol to the reaction mass. A vaporized mixture of the alcohol and water and of unsaponifiable matters originally present in the tall oil is allowed to distill out during the

operation. A temperature of 245° to 270° C. is maintained during the operation, the maximum temperature being reached near the end thereof. As a result, the esterification reaction is about 82% complete.

There is then added about 40 grams of tetrahydrofurfuryl alcohol to the reaction mixture, which is heated for about 7 hours to a temperature above 275° and usually at 290° to 310° C. The temperature is held at the maximum until the acid number has been reduced to about 4.5. The product is then cooled and may be used as such in plasticizer mixtures. However, it is usually preferable to refine the product in order to still further reduce the acid number.

EXAMPLE 2

A mixture is made consisting of 500 grams of water white rosin and 500 grams of the free fatty acids obtained by the splitting of linseed oil. .4% of calcium hydroxide as a catalyst is added thereto. To this mixture is added about 335 grams of tetrahydrofurfuryl alcohol. The mixture is heated under the same conditions as set forth in Example 1 in the two stages there described. After the completion of the reaction, the product having a low acid number is recovered and is refined as usual.

EXAMPLE 3

Coconut oil is split to form free fatty acids and such acids are fractionally distilled to give a fraction consisting essentially of the saturated and unsaturated acids of coconut oil having 14, 16 and 18 carbon atoms. Two mols. of the mixed fatty acids is mixed with 1 mol. of gum rosin and to this is added 2 mols. of tetrahydrofurfuryl alcohol. As a catalyst, .3% of paratoluene sulfonic acid is introduced.

The mixture is heated according to the cycle described in Example 1 and the eventual product is suitably refined.

Various changes may be made in the details of the operation within the spirit of the invention. For instance, in the operation the time and temperature cycle may be varied, as well as the proportions of the several constituents. Different catalysts than those specifically set forth may be used and the operation may be conducted in a single stage. Instead of a batch operation, the process may be made semi-continuous or even fully continuous, with suitable modification in the equipment and in the conditions. Vacuum or pressure may be used if it appears to be desirable. Also an additional stage of esterification may be resorted to in order to reduce the acid number still further. Other monocarboxy acids of the fatty type may be substituted for those specifically named and synthetic fatty acids or branched chain fatty acids may be used. The source of the acids may be of animal or vegetable oils or fats, tallow, waste fats or fatty acids, and others.

There are numerous advantages residing in the present invention, among them being that the raw materials necessary for the operation have been cheap and plentiful. Both of the materials come from vegetable sources, the tall oil from paper-making industries, and the alcohol from distillation of hulls of various grains. Therefore, the supply is plentiful and inexhaustible. The processing is quite simple and does not require complicated apparatus or highly skilled workmen.

It is of extreme importance in a plasticizer that the same have high compatibility with the resinous material to be plasticized. The present plasticizers not only have the high compatibility over an extraordinarily wide range, but over this range exhibit a high efficiency. The mixed esters are completely miscible with each other and, therefore, there is no tendency under any conditions of testing or use for a separation either of the esters from each other or from the plasticized composition. Not only may refined tall oil be used but even crude tall oil has been found suitable and apparently some refining takes place inherently in the esterification operation.

Various compositions containing the plasticizer of the present invention have been made and fully tested. They indicate both high compatibility and high efficiency of the plasticizer. In the following examples, the resin used was a polyvinyl resinous copolymer made by the reaction of approximately 95% vinyl chloride and 5% vinyl acetate. Tests showed the following data.

Example A

100 parts by weight of the vinyl resin were mixed with 43 parts of an ester of tetrahydrofurfuryl alcohol and a tall oil having the following approximate composition:

	Percent
Rosin acids	45
Fatty acids	48
Sterols	6.6

The composition was milled on a standard calender roll, as a result of which it was determined that the surface condition of the composition was smooth, there was no surface tackiness and there was no sweatout of any plasticizer at 295° F. The plasticized composition was molded at 320° F., there being no sweatout of any plasticizer during the operation. The surface appearance remained good.

The load at 100% elongation was 2625 lbs. per square inch when measured in the Scott Tensile Tester model #6L at the rate of 20 inches per minute elongation at room temperature. The composition maintained its plasticity at −10° F. and became brittle at −20° F. The heat loss at 220° F. in a forced draft oven after 4 hours was .35% and after 50 hours was 2.1%.

After aging in the fadeometer, the load at 100% elongation was 2700 lbs. per square inch. There was no sweatout of plasticizer after the aging.

Example B

100 parts by weight of the same resin was mixed with 43 parts of the tetrahydrofurfuryl ester of a distilled tall oil having the following composition:

	Percent
Rosin acids	33–36
Fatty acids	57–62
Sterols	5–7

It was milled as usual and the composition had a smooth surface, did not show any surface tackiness and there was no sweatout at 290° F. It was molded at 320° F., there being no sweatout under the molding conditions and the appearance remained good.

The load at 100% elongation was 2000 lbs. per square inch when measured in the aforesaid Scott Tester. It retained its plasticity at −30° F. and became brittle at −40° F. The heat loss at 220° F. in a forced draft oven after 4 hours was .46% and after 50 hours was 2.9%. After aging in a fadeometer, the load at 100% elongation

was 2150 lbs. per square inch. There was a slight sweatout after 100 hours.

Example C

100 parts of the vinyl resin was mixed with 38.7 parts of the tetrahydrofurfuryl ester of a fractionally distilled tall oil having the following composition:

	Percent
Rosin acid	70
Fatty acids	30

There was also introduced into the mixture 4.3 parts of a plasticizer which is the triethylene glycol ester of a mixture of capric, caproic and caprylic esters. After calendering the surface condition was smooth, there was no surface tack and there was no sweatout at 295° F. After molding at 320° F., the surface appearance remained good and there was no sweatout of plasticizer.

The load at 100% elongation was 2100 lbs. per square inch when measured in the aforesaid Scott Tester. The composition retained its plasticity at −30° F. and became brittle at −40° F. The heat loss of the composition at 220° F. in a forced draft oven after 4 hours was .45% and after 50 hours was 2.7%. After aging in the fadeometer, the load at 100% elongation was 2275 lbs. per square inch. There was a slight sweatout after 100 hours but the sweatout was not substantial.

Example D

The plasticizers of the present invention when mixed with other ester-type plasticizers have unusually higher efficiencies as shown by the following test.

A mixture was made of 100 parts by weight of a polyvinyl resin consisting of the copolymer of 95% vinyl chloride and 5% vinyl acetate (VNYW) with 60 parts of the plasticizer of Example C. On testing it required a load 1400 lbs. per square inch in the Scott Tester to give an elongation of 100%. A mixture was made of 100 parts of the same resin with 60 parts of di-octyl phthalate, which required a load of 775 lbs. per square inch in the Scott Tester to give 100% elongation.

The following mixture was made:

	Parts by weight
Plasticizer of Example C	30
Di-octyl phthalate	30
VNYW resin	100

This mixture required a load of 825 lbs. per square inch in the Scott Tester to give 100% elongation, which is slightly above the load required for the di-octyl phthalate mixture and far below that required for the rosin-fatty acid ester.

Similarly, other ester-type plasticizers, such as monohydric alcohol esters of polybasic fatty acids, dihydric alcohol esters of mono-basic organic acids, and others may be admixed with the tetrahydrofurfuryl esters described above. The amounts of such added plasticizers may range from 2% to 50% of the plasticizer mixture or even more.

Although the invention has been described setting forth several specific embodiments thereof, the invention is not limited thereto as such examples were intended to illustrate the invention. Various changes in the details may be made within the spirit thereof, as for instance, the amount of the plasticizer relative to the resin may be substantially increased above the amounts set forth in such examples. For instance, from 67 to 75 parts of the mixed rosin fatty acid esters may be incorporated in 100 parts of the vinyl chloride resin. In the specification and claims, it is stated that the rosin may be from 30% to 70% of the mixture of acids esterified. These ratios may be varied somewhat and the maximum amount of rosin may be 1% or 2% above the 70% and an equal amount below the lower limit of 30% with the percentage of fatty acids being varied accordingly. The plasticizers of the present invention may be utilized with other vinyl chloride resins than have been specifically described herein. These and other changes in the details may be made within the principles herein set forth and the invention is, therefore, to be broadly construed and not to be limited except by the character of the claims appended hereto.

I claim:

1. A synthetic resinous composition consisting essentially of a polyvinyl chloride-acetate copolymer resin having incorporated therein to 100 parts of resin from 30 to 75 parts of a plasticizer which is the tetrahydrofurfuryl alcohol ester of a mixture of 30–70% of rosin and 70–30% of fatty acids having 10–22 carbon atoms, said plasticizer having an acid number less than 10, said plasticizer containing about 4 parts of the triethylene glycol ester of a mixture of capric, caproic and caprylic acids.

2. A synthetic resinous composition consisting essentially of a polyvinyl chloride-acetate copolymer resin having incorporated therein to 100 parts of resin from 30 to 75 parts of a plasticizer which is a mixture of substantially equal parts of di-octyl phthalate with the tetrahydrofurfuryl alcohol ester of a mixture of 30–70% of rosin and 70–30% of fatty acids having 10–22 carbon atoms, said plasticizer having an acid number less than 10.

EMERY I. VALKO.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,089,375	Humphrey et al.	Aug. 10, 1937
2,339,387	Endres	Jan. 18, 1944

OTHER REFERENCES

Industrial and Engineering Chemistry, articles by Harber et al., vol. 37, pages 953–956, October, 1945.

Modern Plastics, article by Tuttle et al., Dec. 1946, vol. 24, No. 4, pages 163,–166.