Patented May 25, 1937 2,081,407

UNITED STATES PATENT OFFICE

2,081,407

DRIER

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No Drawing. Application April 30, 1936, Serial No. 77,147

11 Claims. (Cl. 134—57)

This invention is a drier and more particularly one adapted to be used in connection with the drying of paints, varnishes and enamels and especially of the character which embodies one or more drying metals, such as cobalt, manganese, iron, and the like, in the form of naphthenates, linoleates and the like.

My experience and research have convinced me that the ideal drier should possess the following prerequisites:

It should remain in perfect solution for an indefinite period of storage.

The metal contained in the driers should be of the highest degree of availability of use.

The drier should have a minimum effect upon the viscosity, flow, color and stability of the clear or pigmented vehicle in which it is incorporated.

The drier should exhibit no adverse action upon the durability of the coating in which it is incorporated.

The drier should not detrimentally affect the color retention properties of the vehicle in which it is used.

The drier should be non-reactive with the pigment portion of paints, varnishes and enamels.

The drier should retain its clarity and homogeneity even when exposed to air.

It should be in such concentrated form as to render it economical from the manufacturers' and shippers' standpoint. For example, it is found practical in cobalt or manganese drier to utilize metal concentrations in the neighborhood of from 4% to 6%.

A cobalt drier should be as blue as possible in order to effect some bleaching action upon the vehicle in which it is used.

A manganese drier should be as pale as possible so as to cause minimum discoloration in paints, varnishes and enamels in which it is incorporated.

One of the most important of the foregoing prerequisites of the ideal drier is that of stability for, unless the drier is stable, it is open to serious disadvantages. For example, it may precipitate out portions of the drying metal, so as to render it impossible to obtain a uniform drying performance. Furthermore, if the drier is unstable, it will not maintain the paint, varnish or enamel in which it is used in a uniform condition and there is a marked tendency to gel, before introduction into the paint, varnish or enamel and to separate from the paint, varnish or enamel after admixture therewith.

For these and other reasons, it has long been recognized that a drier to be commercially practical must, when incorporating most of the drying metals, embody also an appropriate stabilizer and this has been recognized for years and there has grown up in the trade the accepted usage of acids for this purpose, it having been found that excess free acid when incorporated in the drier has a stabilizing function. It may be noted in this connection that common practice has dictated, for this purpose, amounts of acid varying from 2% to as high as 20%, based on the total weight of the solution. While a relatively large number of acids have been used for this purpose, the more commonly employed are naphthenic acids, linseed oil fatty acids, benzoic acid, rosin, etc. Experience has shown, however, that the inclusion of any of these acids as a stabilizing agent in driers introduces a number of serious disadvantages and these disadvantages are fairly well understood in the paint, varnish and enamel business. Those which are outstanding may be briefly enumerated as follows:

The presence of free acid does not as a matter of fact always guarantee permanent stability of the drier solutions. This is particularly true of rosin which, even in higher percentages, will not permanently prevent gellation of a cobalt drier.

The presence of free acids, such as rosin, in a drier, and thus ultimately in paint, varnish and enamel, tends to adversely affect the life of the film for it has been proven that rosin, for example, has a catalytic oxidizing effect upon certain drying oils used therein and this action continues undesirably in the dried film.

The use of free acids, such as linseed oil fatty acids, does not always render the drier immune to skinning when exposed to air.

The addition of sufficient free acid to be effective as a stabilizer in a cobalt drier tends to change the color of the latter from blue to red which is undesirable from a technical as well as a sales standpoint.

The presence of free acids, such as benzoic acid, tends to make the drying performance of the metal uncertain.

Free acid such as benzoic acids are often highly reactive with some of the pigments contained in paint and enamel and such an interaction tends to set up a decided increase in the body of the paint or enamel and tends to impair the tone of some pigments, such as delicate maroon colors.

Under some conditions a drier containing an appreciable amount of free acid will not dry as efficiently with such acid as it would without.

Driers containing free acids exert at times very

pronounced effects upon the physical characteristics of paints, varnishes and enamels causing increase in the viscosity of the paint and impairing the flowing qualities thereof.

The presence of some free acids, such as linseed oil fatty acids, in driers and in the paint vehicle aggravate any tendency of the coating material to after-yellow which is especially noticeable and objectionable in the case of white coatings.

As hereinbefore stated, many of the disadvantages to which reference has been made have been recognized in the industry and much research has been made in an attempt to solve these problems. For example, it has been suggested to use butyl alcohol as a stabilizing agent in place of an acid stabilizer and such butyl alcohol has been employed to some extent. However, while it solves certain of the problems inherent in the use of acid, it introduces certain other problems which are even more serious in some respects. For example, butyl alcohol is highly volatile and the drier must be used almost immediately to obtain any satisfactory results. If left uncovered it evaporates very rapidly and the stabilizing action is correspondingly decreased. It may also be noted that butyl alcohol and other volatile stabilizers have a decided effect upon the viscosity of the paint, varnish or enamel vehicles and this too is undesirable. Experience has definitely shown that it is a practical impossibility to obtain uniform stabilizers with butyl alcohol for obvious reasons.

With the foregoing considerations in mind, it will be clear that a very definite need existed in the industry for a concentrated drier which will embody the ideal conditions to which I have referred and without the detrimental features adverted to. The object of the present invention was to produce such a drier.

I have found that metal driers of the character described may be very appreciably improved and in some cases made practically ideal through the employment of a stabilizing agent which is non-volatile, neutral, substantially water-insoluble and non-reactive with the vehicle or pigments in which the drier is to be used and which has no noticeable effect upon the viscosity of the paint to which they may be added. For example, I have obtained very satisfactory results with stabilizers having the properties of triethyl citrate, tributyl citrate, cyclo-hexyl-paratoluene-sulfanamid particularly when employed in connection with naphthenate metal driers. These specified stabilizers materially increase the solubility of the cobalt naphthenate in the mineral spirits and materially promote solubility in the combination and produce that permanent solubility so essential to an ideal drier. They are non-volatile and neutral and thus will not volatilize off from the finished dried during storage, and that attendant reaction which is so detrimental in acid stabilizers is entirely absent in the stabilizers to which I have referred.

The amount of stabilizer needed is so small as not to affect the physical properties of the paints, varnishes or enamels and a drier carrying from 4% to 6% cobalt, for example, has been found stable and efficient over long periods of time.

Other features and advantages of the invention will hereinafter appear in connection with the following illustrative examples showing how driers embodying this invention have been practically produced.

Example No. 1

To 440 pounds of a suitable naphthenic acid there was added 9 pounds of cyclo-hexyl-paratoluene-sulfanamid. This was done with accompanying agitation. To this was added, with accompanying agitation, a solution carrying 88 pounds of flake caustic soda dissolved in 400 pounds of water. To the resulting alkali-soap solution was added 464 pounds of mineral spirits under thorough agitation. While the agitation was continued, there was finally introduced a solution of 295 pounds cobalt sulfate crystals in 400 pounds of water. The mixture was thereupon allowed to stratify and it was found that such stratification occurred promptly and was sharply defined. The supernatant liquid carrying a drier was decanted off and yielded 1,000 pounds of 6% cobalt naphthenate solution containing approximately 1% of stabilizer. The above procedure may be carried out at room temperature, but can be speeded up at slightly elevated temperatures.

In lieu of the stratification and subsequent decantation referred to, it has been found thoroughly practical to mechanically separate in any appropriate way as by centrifuging.

Example No. 2

A similar procedure may be carried out using approximately 27 pounds of the triethyl citrate in place of the 9 pounds of cyclo-hexyl-paratoluene-sulfanamid.

Example No. 3

A similar procedure may be carried out using approximately 27 pounds of the tributyl citrate in place of the 9 pounds of cyclo-hexyl-paratoluene-sulfanamid.

Example No. 4

A 6% manganese naphthenate solution containing triethyl citrate as stabilizer was prepared by adding to 450 pounds of naphthenic acid 28 pounds of triethyl citrate with good agitation. Then a solution of 90½ pounds of caustic soda in 400 pounds of water was introduced under continued agitation. To the thus obtained alkali-soap-solution was added 487 pounds of mineral spirits and finally, while agitation was continued, a solution of 217 pounds manganese sulfate in 400 pounds of water was introduced. The resulting solution was found to stratify rapidly and completely and was mechanically separated and it was found that the yield was approximately 1,000 pounds of 6% manganese naphthenate drier containing 2.8% of the stabilizer. The use of moderate heats will speed up the operation.

It is also possible to operate with more than one stabilizer, as will be apparent from the following example.

Example No. 5

6% manganese naphthenate solution was obtained by following the procedure specified in Example 4, by using a mixture of 19 pounds triethyl citrate and 5 pounds of cyclo-hexyl-paratoluene-sulfanamid instead of the 28 pounds of triethyl citrate only mentioned in Example 4. The resulting solution stratified rapidly and cleanly, the supernatant liquid was readily mechanically separated giving a yield of 1,000 pounds of 6% manganese naphthenate containing a total 2.45% combined stabilizer.

Example No. 6

A 6% iron naphthenate solution containing tributyl citrate as stabilizer was prepared by adding to 488 pounds of a suitable naphthenic acid 30 pounds of tributyl citrate. This was done under thorough agitation. To this was added under agitation 97 pounds of flake caustic soda dissolved in 400 pounds of water. To the resultant alkali soap solution was added 420 pounds of mineral spirits. While the agitation was continued, there was finally introduced a solution of 337 pounds of iron sulphate in 400 pounds of water. The reaction mixture was thereupon allowed to stratify and it was found that such stratification occurred promptly and was sharply defined. The supernatant liquid was found to yield 1,000 pounds of a 6% iron naphthenate solution containing approximately 3% of stabilizer.

Example No. 7

A 6% solution of copper naphthenate containing triethyl citrate as stabilizer was prepared by adding 30 pounds of triethyl citrate to 421 pounds of a suitable naphthenic acid with good agitation. Then a solution of 84 pounds of flake caustic soda in 400 pounds of water was added with thorough stirring. To the thus obtained alkali soap solution was added 481 pounds of mineral spirits and finally, while agitation was continued, a solution of 245 pounds of copper sulphate in 400 pounds of water. The resultant solution was found to stratify rapidly and was mechanically separated and it was found that the yield was approximately 1,000 pounds of 6% copper naphthenate solution containing 3% of stabilizer.

In all of the foregoing examples, I have set forth practical methods of producing metal naphthenates with stabilizers of the character under consideration through the process of double decomposition. This process gives highly satisfactory results, but is not the only procedure which may be followed. On the contrary, it is entirely feasible to use any well known procedure known to the art for the making of naphthenate driers of the kind herein under consideration, but the stabilizer or stabilizers to be employed should be incorporated into the drier by incorporation into the acid or into the acid mineral spirits solution before proceeding with the necessary chemical reactions which are involved in the production of metallic driers.

Furthermore the foregoing examples deal with the making of metal naphthenate driers, but the invention may be carried out in the production of metallic driers of other acids of which the following may be referred to by way of example.

Example No. 8

A 4% cobalt linoleate solution was prepared by adding 18 pounds of tributyl citrate to 430 pounds of a suitable linseed oil fatty acid with attendant agitation. While agitation was continued there was introduced a solution of 55 pounds of flake caustic soda in 300 pounds of water. Finally, while agitation was continued there was added 198 pounds of cobalt sulphate dissolved in 300 pounds of water. The resulting reaction mixture was allowed to separate and it was found that such stratification occurred promptly and was sharply defined. The supernatant liquid carrying a drier was decanted off and yielded approximately 1,000 pounds of a 4% cobalt linoleate solution containing 2% of stabilizer.

While the driers which have thus far been enumerated in the examples given are liquid driers, carrying volatile solvents, these solvents may be driven off in any appropriate way to yield driers in solid form, or, if desired, paste driers may be produced by leaving some of the solvent in the drier or by adding any appropriate vehicle as will be well understood.

Driers made in the manner hereinbefore described are superior to driers heretofore used in the art. They are efficient, economical and uniform in their operation. They are permanent in character. They act expressly and solely as catalytic drying agents upon paint, varnish and enamel vehicles in which they are incorporated and exert no detrimental influence thereon.

Reference is made to the fact that the triethyl citrate and cyclo-hexyl-paratoluene-sulfanamid stabilizers of this invention are practically insoluble in petroleum hydrocarbons and more particularly mineral spirits which are commonly used as a solvent or diluent for driers and for paints, varnishes and enamels in which they are incorporated. Yet I have found that when incorporated in relatively small percentages in, for example, cobalt-naphthenate-metal spirits driers that they produce a remarkable stabilizing effect.

Having thus fully described the invention, what I claim as new and desire to secure by Letters Patent is:

1. A drier comprising a water-insoluble soap of a drying metal and an organic alcohol derivative stabilizer selected from the group which consists of triethyl citrate, tributyl citrate and cyclo-hexyl-paratoluene-sulfanamid.

2. A drier comprising cobalt naphthenate and an organic alcohol derivative stabilizer selected from the group which consists of triethyl citrate, tributyl citrate and cyclo-hexyl-paratoluene-sulfanamid.

3. A drier comprising a water-insoluble manganese soap and an organic alcohol derivative stabilizer selected from the group which consists of triethyl citrate, tributyl citrate and cyclo-hexyl-paratoluene-sulfanamid.

4. A drier comprising a water-insoluble iron soap and an organic alcohol derivative stabilizer selected from the group which consists of triethyl citrate, tributyl citrate and cyclo-hexyl-paratoluene-sulfanamid.

5. A drier comprising a water-insoluble soap of a drying metal dissolved in an organic thinner which solution contains an organic alcohol derivative stabilizer selected from the group which consists of triethyl citrate, tributyl citrate and cyclo-hexyl-paratoluene-sulfanamid.

6. A drier comprising a neutral, water-insoluble soap of a drying metal dissolved in an organic thinner which solution contains an organic alcohol derivative stabilizer selected from the group which consists of triethyl citrate, tributyl citrate and cyclo-hexyl-paratoluene-sulfanamid.

7. A drier comprising a metal naphthenate dissolved in an organic thinner and which solution contains an organic alcohol derivative stabilizer selected from the group which consists of triethyl citrate, tributyl citrate and cyclo-hexyl-paratoluene-sulfanamid.

8. A drier comprising cobalt naphthenate dissolved in an organic thinner and which solution contains an organic alcohol derivative stabilizer selected from the group which consists of triethyl citrate, tributyl citrate and cyclo-hexyl-paratoluene-sulfanamid.

9. A drier comprising manganese naphthenate dissolved in an organic thinner and which solu-

tion contains an organic alcohol derivative stabilizer selected from the group which consists of triethyl citrate, tributyl citrate and cyclo-hexyl-paratoluene-sulfanamid.

10. A drier comprising iron naphthenate dissolved in an organic thinner and which solution contains an organic alcohol derivative stabilizer selected from the group which consists of triethyl citrate, tributyl citrate and cyclo-hexyl-paratoluene-sulfanamid.

11. A drier comprising a water-insoluble cobalt soap and an organic alcohol derivative stabilizer selected from the group which consists of triethyl citrate, tributyl citrate, and cyclo-hexyl-paratoluene-sulfanamid.

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