

UNITED STATES PATENT OFFICE

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STABILIZED SOLUTIONS OF SICCATIVES

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The present invention relates to stabilized solutions of siccative.

Solutions of siccatives in white spirit, benzene, oil of turpentine or other volatile solvents as a rule tend to exhibit sedimentation (to "deposit") when allowed to stand for some time. The manner in which deposits occur or the form they assume depends on the nature and the quantity of the volatile solvent used, but according to my observations is dependent in the first line on the kind and quantity of the metal contained in the siccative and it is approximately proportional to the capability of these metals of accelerating the drying process. The formation of sediments therefore differs considerably in the various naphthenates, linoleates and resinates. The tendency to sedimentation is the most pronounced in the cobalt driers, next range the manganese driers, lead driers, zinc driers and calcium driers. Corresponding to the high metal content, the tendency of sedimentation is greatest in the naphthenates and the smallest in the resinates, particularly in the molten resinates. In the process of sedimenting or gelatinizing of the solutions the siccatives behave in a marked manner as colloids, as in general the siccatives in volatile solvents are forming only colloidal, and not molecular solutions. These colloids are of a lyophile nature; they are thus inclined to swell in the solvents. In the case of cobalt naphthenate, having a high content of active siccative metal, the transition from the sol-state into the gel-state is the most rapid and extensive and gelatinization throughout the entire mass is of frequent occurrence. These sedimentations and gelatinizations are extremely undesirable, inasmuch as they cannot be reversed by the consumer. Once gelatinization has taken place, the consumer succeeds only exceptionally to redissolve by again heating the mass with the liquid which remained, even when replenished by the addition of evaporated volatile solvent. In spite of the aid of fresh solvent, no re-dissolution at all or only temporary re-dissolutions of the precipitates can be obtained.

I have now ascertained that these incon-

veniences can be overcome, i. e. that the sedimentation and gelatinizing of the solutions of siccatives can be prevented by the addition to such solutions of relatively small quantities of free carboxylic acids of the unsaturated aliphatic or of the aromatic series as protective agents. There may be used as protective agents for instance the olefinic acids, such as acrylic acid, crotonic acid or linoleic acid, furthermore the free acids contained in other drying or semidrying oils, such as perillic acid; furthermore the aromatic carboxylic acids, the homologues and substitution products thereof, such as benzoic acid, carboxylic acids of the benzene series, such as amino-benzoic acid, or the derivatives, such as hippuric acid, phthalic acid, cinnamic acid, naphthoic acid.

The more the siccative metals in the solution of the siccatives are capable of accelerating the drying process, the greater are the proportions of the unsaturated fatty acids which may advantageously be added to the solution. By the addition of these carboxylic acids the stability of the colloidal solutions is considerably increased which effect may clearly be seen in the viscosity remaining constant.

There may, for instance, be used about the following quantities of free unsaturated fatty acids calculated upon the solid drier:

	Per cent
With pure cobalt driers.....	15-20
With manganese-cobalt driers.....	10-15
With cobalt-zinc driers and cobalt-lead driers.....	3-5

in the case of naphthenates and linoleates the upper limit and in the case of resinates the lower limit is the most advantageous.

The solutions of siccatives thus prepared may be stored for any length of time without showing any sediments or gelatinizations. This surprising effect of the free fatty acids, for instance of the linoleic acid, was by no means to be foreseen, the more so as depositing, especially of the driers containing lead and zinc, is caused already by small quantities of free fatty acids in boiled linseed oil, or similar oils, containing said siccatives.

Furthermore the use of free benzoic acid involves the special advantage that free benzoic acid is particularly capable of dissolving the siccatives if organic volatile solvents are present. The addition of free benzoic acid not only prevents the gelatinization of such solutions, but also conversely enables even completely inspissated solutions to reconvert into highly fluid completely homogeneous solutions, which process takes place to some extent even at ordinary temperature. By the addition of benzoic acid gelatinized solutions can be reconverted into workable condition.

The free carboxylic acids may be added either during the preparation of the solid siccatives or prior to dissolving same in volatile solvents.

For the purpose in question even small quantities of an aromatic carboxylic acid are already sufficient for preventing the mass from gelatinizing; in the case of benzoic acid, for instance, only about 25 per cent of the quantity of linoleic acid mentioned above need be added. Larger quantities have, however, by no means a detrimental effect. By the addition of benzoic acid the capability of the siccatives of accelerating the drying process is still increased compared with the addition of linoleic acid. The viscosity is likewise considerably reduced thereby. The viscosities of a siccative without any of the above mentioned additional substances, of a siccative containing 20 per cent of linoleic acid and of a siccative containing 5 per cent of benzoic acid stand in a proportion of about 5:2:1.

In the following examples the proportion of 1 part of the siccative to 4 parts of the volatile solvent (i. e. a content of 20 per cent of siccative) has been chosen as that which is the most used for solutions of siccatives. The formation of precipitates is, however, likewise not to be feared, if more diluted or more concentrated solutions are prepared.

The following examples serve to illustrate my invention, but they are not intended to limit it thereto:

(1) 100 kgs. of solid cobalt naphthenate are gradually caused to melt in a container at about 140° C. As soon as the fused mass is completely liquid, 380 kgs. of white spirit are added in a thin stream, while further vigorously stirring. 20 kgs. of linoleic acid are then run in and stirring is continued until a completely uniform solution is obtained. In order to remedy the inflammability of solutions of this kind, one-quarter of the white spirit, or more, is suitably replaced by carbon tetrachloride or other halogenated hydrocarbons.

(2) 100 kgs. of solid manganese linoleate in pieces as small as possible are gradually introduced, while well stirring, into 385 kgs. of oil of turpentine previously heated to a temperature between 140° C. and 150° C. Stir-

ring is continued until the solid drier has completely dissolved. After the solution has been allowed to cool, any oil of turpentine lost by volatilization is added again and in order to prevent the solution from gelatinizing, 15 kgs. of arachidic acid are introduced, while stirring.

(3) 100 kgs. of solid cobalt-lead resinate are dissolved in the cold or at a moderate temperature in 400 kgs. of a usual volatile solvent. 3 kgs. of linoleic acid are then introduced, while stirring.

(4) In a vessel which can be tightly closed 275 kgs. of a mixture of hydrocarbons of the terpene series, 120 kgs. of benzene and 5 kgs. of perillic acid are poured on 75 kgs. of zinc naphthenate and 25 kgs. of cobalt linoleate; the whole is stirred or agitated from time to time at ordinary temperature until the driers have completely dissolved which will occur after about 4 hours. The solution obtained will keep free from sedimentation and has no tendency to gelatinize.

(5) About 400 kgs. of white spirit or of another volatile solvent are run in a thin stream at about 130° C., while stirring, into 100 kgs. of precipitated and washed cobalt naphthenate which have been dehydrated. When the temperature has fallen below 100° C., 6 kgs. of benzoic acid are gradually added and stirring is continued until the solution is completely uniform.

(6) 100 kgs. of manganese linoleate are heated until a uniform melt is obtained. There are then introduced in the manner, as described in Example 1, 400 kgs. of sangajol (a fraction of petroleum hydrocarbons boiling within the limits of 150 to 190° C.), while simultaneously adding 5 kgs. of ortho-amino benzoic acid.

(7) 100 kgs. of cobalt-zinc resinate are dissolved by gently heating in 400 kgs. of oil of turpentine, and 3 kgs. of phthalic acid are then added thereto.

(8) 100 kgs. of cobalt-manganese naphthenate in small pieces are placed in a vessel which can be closed tightly. 3 kgs. of benzaldehyde and 3 kgs. of hippuric acid are added thereto and on the mixture there are poured 900 kgs. of a mixture of volatile hydrocarbons of the terpene series and agitated or intimately stirred at ordinary temperature until the solid drier has completely dissolved which can easily be attained in about 3-4 hours, as the aromatic carboxylic acids capable of preventing the gelatinization simultaneously possess the peculiarity of promoting the dissolution.

For sake of simplification I have designed, in the following claims, the solutions according to my invention, i. e. not depositing and not gelatinizing solutions by the term "stabilized solutions".

I claim:

1. As a new composition of matter, a sta-

- bilized solution consisting of a siccative, a volatile solvent and an organic carboxylic acid of the group consisting of aromatic carboxylic and unsaturated aliphatic acids.
- 5 2. As a new composition of matter, a stabilized solution consisting of a siccative, a volatile solvent and an unsaturated aliphatic carboxylic acid.
- 10 3. As a new composition of matter, a stabilized solution consisting of a siccative, a volatile solvent and linoleic acid.
- 15 4. As a new composition of matter, a stabilized solution consisting of a siccative, a volatile solvent and an unsaturated organic carboxylic acid in a quantity ranging from 3 to 20 per cent of the siccative.
- 20 5. As a new composition of matter, a stabilized solution consisting of a siccative, a volatile solvent and an unsaturated aliphatic carboxylic acid in a quantity ranging from 3 to 20 per cent of the siccative.
- 25 6. As a new composition of matter, a stabilized solution consisting of a siccative, a volatile solvent and linoleic acid in a quantity ranging from 3 to 20 per cent of the siccative.
- 30 7. As a new composition of matter, a stabilized solution consisting of a siccative, a volatile solvent and an unsaturated aliphatic carboxylic acid in a quantity ranging from 15 to 20 per cent of the siccative.
- 35 8. As a new composition of matter, a stabilized solution consisting of a siccative, a volatile solvent and linoleic acid in a quantity ranging from 15 to 20 per cent of the siccative.
- 40 9. As a new composition of matter, a stabilized solution consisting of a siccative, a volatile solvent and linoleic acid in a quantity of about 20 per cent of the siccative.
- 45 10. As a new composition of matter, a stabilized solution consisting of a siccative, a volatile solvent and an aromatic carboxylic acid.
- 50 11. As a new composition of matter, a stabilized solution consisting of a siccative, a volatile solvent and an aromatic carboxylic acid of the benzene series.
- 55 12. As a new composition of matter, a stabilized solution consisting of a siccative, a volatile solvent and an aromatic carboxylic acid in a quantity ranging from 3 to 6 per cent of the siccative.
- 60 13. As a new composition of matter, a stabilized solution consisting of a siccative, a volatile solvent and an aromatic carboxylic acid of the benzene series in a quantity ranging from 3 to 6 per cent of the siccative.
- 65 14. As a new composition of matter, a stabilized solution consisting of a siccative, a volatile solvent and an aromatic carboxylic acid in a quantity of about 6 per cent of the siccative.
15. As a new composition of matter, a stabilized solution consisting of a siccative, a volatile solvent and an aromatic carboxylic acid of the benzene series in a quantity of about 6 per cent of the siccative.
16. As a new composition of matter, a stabilized solution consisting of a siccative, a volatile solvent and benzoic acid in a quantity of about 6 per cent of the siccative.
17. As a new composition of matter, a stabilized solution consisting of a siccative, a volatile solvent and benzoic acid in a quantity of about 6 per cent of the siccative.
18. As a new composition of matter, a stabilized solution consisting of a siccative, a volatile solvent and amino-benzoic acid in a quantity of about 5% of the siccative.
19. As a new composition of matter, a stabilized solution consisting of a siccative, a volatile solvent and phthalic acid in a quantity of about 3% of the siccative.
20. As a new composition of matter, a stabilized solution consisting of 20 per cent of a siccative, an unsaturated carboxylic acid in a quantity ranging from 3 to 20 per cent of the siccative, the balance being a volatile solvent.
- In testimony whereof, I affix my signature.
FRIEDRICH MEIDERT.

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