Patented Mar. 30, 1937 2,075,230

UNITED STATES PATENT OFFICE

2,075,230

PRODUCTION OF SICCATIVES

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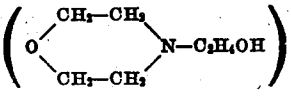
No Drawing. Application September 12, 1931, Serial No. 562,602. In Germany October 21, 1930

15 Claims. (Cl. 134—57)

The present invention relates to the production of siccatives.

It is well known that the most important constituent of the dryers employed in the lacquer and varnish industries, the so-called siccatives, is the metal combined with an organic acid of high molecular weight, while the organic acid generally speaking plays an unimportant part. Since every siccative is looked upon as a foreign body in the varnish or lacquer, those siccatives are preferred in the industry which have a high content of metal in the molecule and which therefore can be employed in small amounts. Suitable siccatives are for example the oleates, linoleates, resinates, naphthenates and the like carboxylic acids containing at least 7 carbon atoms obtainable from acids of vegetal, i. e. vegetable or animal origin such as oleic acid, linoleic acid, palmitic acid, resinic acids, such as colophony, or of mineral or synthetic origin such as naphthenic acid fractions containing at least 7 carbon atoms, benzoic, cinnamic, partially hydrogenated benzoic and like carboxylic acids containing from 7 to 30 carbon atoms by conversion with one or more compounds of base metals capable of forming water-insoluble salts with the said acids, i. e. of the alkaline earth or heavy metals, singly or in combination, as for example of calcium, barium, strontium, magnesium, cerium, thorium, cobalt, lead, manganese, zinc, cadmium, vanadium, chromium, iron, copper, and aluminium. The above mentioned metals are hereinafter referred to as "siccative base metals". Valuable siccatives may also be obtained for example according to the British patent, No. 311,716, from the carboxylic acids formed, by the destructive oxidation of paraffin hydrocarbons such as paraffin wax or paraffin oil. Furthermore the products containing heavy metal salts of sulphonic acids prepared from petroleum oils by treatment with fuming sulphuric acid or sulphuric anhydride according to the U. S. Patent No. 1,686,484, are also suitable as siccatives. In most cases the best siccatives are obtained from carboxylic acids containing from 7 to 18 carbon atoms.

I have now found that siccatives having remarkable properties are obtained, when the usual preparation of siccatives by the conversion of the said or equivalent organic acids containing at least 7 carbon atoms preferably from 7 to 20 carbon atoms, or of their alkali metal salts, with one or more salts, hydroxides or oxides of the base metals capable of forming water-insoluble salts with the said acids, i. e. alkaline earth or heavy metals, especially of lead, cobalt or manganese or of mixtures thereof with each other or with those of other metals referred to above, is carried out in the presence of amines. The said base metal compounds are preferably employed in more than equimolecular proportions calculated on the quantity of acid component employed. The quantities of the base metal compounds in excess of the said theoretical quantities may vary within wide limits and depend to some degree on the nature and quantity of the amine employed. Generally, an excess of from 0.5 per cent to 50 per cent of the molecular quantities may be employed. In most cases, however, I prefer excess quantities of from 1 or 3 to 35 per cent. Suitable amines are for example ethylamine, ethylene diamine, aniline, hexamethylene tetramine, dimethyl or diethyl anilines, benzyl amine, quinoline, pyridine and like primary, secondary or tertiary amines. Amines containing at least one organic radicle having a hydroxyl group, p-amino phenol and especially alkylol amines as for example mono-, di- and tri-ethanol amines or propanol amines and their commercial mixtures and alkyl-ethers thereof such as mono- or di-hydroxy ethyl ethers of triethanol amine or N-hydroxyethyl morpholine



give particularly good results. Generally speaking, the siccatives prepared according to the present invention have a considerably higher metal content than those prepared in the absence of amines, the amines apparently taking part in the reaction and forming chemical combinations with the acids and the base metals. Thus for example a cobalt naphthenate prepared in the usual manner contains from about 12 to 12.5 per cent by weight of cobalt while a cobalt naphthenate prepared according to this invention with the aid of triethanolamine contains from about 15.5 to 16 per cent of cobalt. The quantity of amine employed usually corresponds to about 1 molecular proportion of amine to about 2 molecular proportions of the acid employed but also lower quantities say one half of that stated, or higher quantities say up to 1½ molecular proportions may be employed, the highest content of base being usually obtained with about 1 molecular proportion of amine per 2 molecular proportions of acid.

The siccatives prepared according to the present invention, after fusion, are hard and several of them may even be pulverized without their

sticking together again. In part they may be obtained as a powder, as for example by precipitation of an aqueous solution of an alkali metal salt of fatty acid of high molecular weight with an aqueous solution of a metal salt at room temperature. The siccatives do not oxidize in the air. They retain their original color and readily dissolve at from 100° to 130° C. in linseed oil to give clear solutions. The said siccatives readily dissolve in the cold in the volatile solvents usually employed in the lacquer and varnish industries, to give clear solutions even in the proportions of 1:1. The resulting solutions do not gelatinize even in the absence of protective colloids. The said solutions do not oxidize and they retain their original color. Because of their increased metal content, smaller amounts of the said siccatives are necessary in the preparation of varnishes and lacquers than of the usual siccatives.

The following examples will further illustrate the nature of this invention but the invention is not restricted to these examples. The parts are by weight.

Example 1

100 parts of naphthenic acid are saponified in the usual manner at about 100° C. with an aqueous solution of 20.5 parts of caustic soda. 40 parts of commercial triethanolamine (a mixture of triethanolamine with mono- and diethanolamines) are added to the soap solution and the whole is precipitated with an aqueous solution of 90 parts of cobalt sulphate at the boiling temperature. The precipitate is washed a few times with hot water and then dehydrated in the usual manner by fusion. The product thus obtained contains about 16% by weight of cobalt, whereas, if no amine is employed and the other conditions are observed, a product is obtained which contains only about 12% by weight of cobalt.

Example 2

100 parts of naphthenic acid are saponified in the manner described in Example 1. 75 parts of commercial triethanolamine are added to the cooled soap solution and the whole is precipitated with an aqueous solution of 120 parts of aluminium sulphate in the cold. The precipitate is washed a few times with water, dried at about 60° C. and if necessary pulverized. The product thus obtained contains about 8% by weight of aluminium, whereas, if no amine is employed and the other conditions are observed, a product is obtained which contains only about 4.5% by weight of aluminium.

Example 3

100 parts of colophony are saponified in the usual manner with 14 parts of caustic soda. 45.5 parts of the mono-hydroxy ethyl ether of triethanolamine (obtainable for example by acting with ethylene oxide on an aqueous solution of an about equimolecular proportion of triethanolamine) are added to the soap solution and the whole is precipitated with an aqueous solution of 20 parts of crystalline cobalt sulphate and 50 parts of crystalline zinc sulphate at about 50° C. The precipitate is washed a few times with water and dried at about 60° C. and powdered.

Example 4

100 parts of a liquid mixture of fatty acids obtained by the destructive oxidation of soft paraffin wax by blowing with air at 160° C. are saponified at 100° C. with 20 parts of caustic soda; 15 parts of ethylene diamine are added to the soap solution and the whole is precipitated with an aqueous solution of 100 parts of crystalline lead acetate (sugar of lead) and 30 parts of an aqueous solution of crystalline cobalt sulphate at the boiling temperature. The precipitate is washed a few times with hot water and dehydrated by fusion. The product may be pulverized if desired. The product thus obtained contains about 34% by weight of lead and 4.5% by weight of cobalt, whereas, if no amine is employed and the other conditions are observed, a product is obtained which contains only about 25% by weight of lead and 2.5% by weight of cobalt.

Example 5

100 parts of naphthenic acid are saponified as described in Example 1. 19 parts of pyridine are added to the soap solution and the whole is precipitated with an aqueous solution of 82.5 parts of cobalt sulphate. The precipitate is washed a few times with hot water and then dehydrated in the usual manner by fusion. Instead of the pyridine 30 parts of quinoline may be employed. The product thus obtained contains about 15% by weight of cobalt, whereas, if no amine is employed and the other conditions are observed, a product is obtained which contains only about 12% by weight of cobalt.

Example 6

100 parts of naphthenic acid are heated to 200° C. together with 40 parts of triethanolamine, whereupon 33 parts of cobalt hydroxide are gradually added and the whole is heated to about 220° C. until the hydroxide is completely dissolved. After cooling the melt the product may be pulverized. The product thus obtained contains about 16% by weight of cobalt, whereas, if no amine is employed and the other conditions are observed, a product is obtained which contains only about 12% by weight of cobalt.

Example 7

100 parts of naphthenic acid are saponified in the usual manner at about 100° C. with an aqueous solution of 20.5 parts of caustic soda. 22 parts of aniline are added to the soap solution and the whole is precipitated with an aqueous solution of 105 parts of crystalline lead acetate at the boiling temperature. The precipitate is washed a few times with hot water and then dehydrated in the usual manner by fusion. The product thus obtained contains from 42% to 43% by weight of lead, whereas, if no amine is employed and the other conditions are observed, a product is obtained which contains only from 33% to 34% by weight of lead.

What I claim is:—

1. In the production of siccatives from organic acids containing at least 7 carbon atoms and an at least equimolecular proportion of salts of "siccative base metals" capable of forming water-insoluble salts with the said acids, the step which comprises carrying out the reaction in the presence of an amine the latter being employed in an amount of from one half to one and a half molecular proportions calculated on 2 molecular proportions of said acids, any water-soluble salts still present being washed out from the reaction product.

2. In the production of siccatives from organic acids containing at least 7 carbon atoms and an at least equimolecular proportion of salts of "siccative base metals" capable of forming water-

insoluble salts with the said acids, the step which comprises carrying out the reaction in the presence of an alkylol amine the latter being employed in an amount of from one half to one and a half molecular proportions calculated on 2 molecular proportions of said acids, any water-soluble salts still present being washed out from the reaction product.

3. A siccative comprising at least one water-insoluble combination of an organic acid containing at least 7 carbon atoms with an amine, said amine being present in said combination in an amount of from one half to one and a half molecular proportions calculated on 2 molecular proportions of said acid, and a "siccative base metal" capable of forming a water-insoluble salt with said acid, said base metal being present in said combination in a quantity exceeding that theoretically corresponding to a salt of said metal with said acid.

4. A siccative comprising at least one water-insoluble combination of an organic acid containing from 7 to 30 carbon atoms with an amine, said amine being present in said combination in an amount of from one half to one and a half molecular proportions calculated on 2 molecular proportions of said acid, and a "siccative base metal" capable of forming a water-insoluble salt with said acid, said base metal being present in said combination in a quantity exceeding that theoretically corresponding to a salt of said metal with said acid.

5. A siccative comprising at least one water-insoluble combination of an organic acid of vegetal origin with an amine, said amine being present in said combination in an amount of from one half to one and a half molecular proportions calculated on 2 molecular proportions of said acid, and a base metal capable of forming a water-insoluble salt with said acid, said "siccative base metal" being present in said combination in a quantity exceeding that theoretically corresponding to a salt of said metal with said acid.

6. A siccative comprising at least one water-insoluble combination of a naphthenic acid containing at least 7 carbon atoms with an amine, said amine being present in said combination in an amount of from one half to one and a half molecular proportions calculated on 2 molecular proportions of said acid, and a "siccative base metal" capable of forming a water-insoluble salt with said acid, said base metal being present in said combination in a quantity exceeding that theoretically corresponding to a salt of said metal with said acid.

7. A siccative comprising at least one water-insoluble combination of an organic acid containing at least 7 carbon atoms with an aliphatic amine, said amine being present in said combination in an amount of from one half to one and a half molecular proportions calculated on 2 molecular proportions of said acid, and a "siccative base metal" capable of forming a water-insoluble salt with said acid, said base metal being present in said combination in a quantity exceeding that theoretically corresponding to a salt of said metal with said acid.

8. A siccative comprising at least one water-insoluble combination of an organic acid containing at least 7 carbon atoms with an aliphatic-aromatic amine, said amine being present in said combination in an amount of from one half to one and a half molecular proportions calculated on 2 molecular proportions of said acid, and a "siccative base metal", capable of forming a water-insoluble salt with said acid, said base metal being present in said combination in a quantity exceeding that theoretically corresponding to a salt of said metal with said acid.

9. A siccative comprising at least one water-insoluble combination of an organic acid containing at least 7 carbon atoms with an alkylol amine, said amine being present in said combination in an amount of from one half to one and a half molecular proportions calculated on 2 molecular proportions of said acid, and a "siccative base metal" capable of forming a water-insoluble salt with said acid, said base metal being present in said combination in a quantity exceeding that theoretically corresponding to a salt of said metal with said acid.

10. A siccative comprising at least one water-insoluble combination of an organic acid containing at least 7 carbon atoms with an ethanol amine, said amine being present in said combination in an amount of from one half to one and a half molecular proportions calculated on 2 molecular proportions of said acid, and a "siccative base metal" capable of forming a water-insoluble salt with said acid, said base metal being present in said combination in a quantity exceeding that theoretically corresponding to a salt of said metal with said acid.

11. A siccative comprising at least one water-insoluble combination of an organic acid containing at least 7 carbon atoms with a mixture of alkylol amines, said amines being present in said combination in an amount of from one half to one and a half molecular proportions calculated on 2 molecular proportions of said acid, and a "siccative base metal" capable of forming a water-insoluble salt with said acid, said base metal being present in said combination in a quantity exceeding that theoretically corresponding to a salt of said metal with said acid.

12. A siccative comprising at least one water-insoluble combination of a naphthenic acid containing at least 7 carbon atoms with an aniline base, said amine being present in said combination in an amount of from one half to one and a half molecular proportions calculated on 2 molecular proportions of said acid, and at least one base metal selected from the group consisting of lead, manganese and cobalt, base metals being present in said combination in a quantity exceeding that theoretically corresponding to a salt of said metal with said acid.

13. A siccative comprising at least one water-insoluble combination of a naphthenic acid containing at least 7 carbon atoms with an alkylol amine, said amine being present in said combination in an amount of from one half to one and a half molecular proportions calculated on 2 molecular proportions of said acid, and at least one base metal selected from the group consisting of lead, manganese and cobalt, base metals being present in said combination in a quantity exceeding that theoretically corresponding to a salt of said metal with said acid.

14. A siccative comprising at least one water-insoluble combination of a naphthenic acid containing at least 7 carbon atoms with triethanolamine, said amine being present in said combination in an amount of from one half to one and a half molecular proportions calculated on 2 molecular proportions of said acid, and at least one base metal selected from the group consisting of lead, manganese and cobalt, base metals being present in said combination in a quantity

exceeding that theoretically corresponding to a salt of said metal with said acid.

15. A siccative comprising at least one water-insoluble combination of a naphthenic acid containing at least 7 carbon atoms with triethanolamine, said amine being present in said combination in an amount of from one half to one and a half molecular proportions calculated on 2 molecular proportions of said acid, and at least one base metal selected from the group consisting of lead, manganese and cobalt, base metals being present in a quantity exceeding from 3 to 35 per cent the quantity theoretically corresponding to the salts of said metals with said acid.

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