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3,723,152

DRYING OIL COMPOSITIONS, COBALT DRIER COMPOSITIONS THEREFOR AND PROCESS OF MAKING SAME

Anthony Alkaitis, Cleveland Heights, and Gordon A. Thomas, Rocky River, Ohio, assignors to Mooney Chemicals, Inc., Cleveland, Ohio

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10 Claims

ABSTRACT OF THE DISCLOSURE

Basic cobalt salts of neodecanoic acid have a stoichiometric excess of cobalt relative to that acid, as compared with neutral cobaltous salt of the acid, and are oil-soluble. Thus they are useful with hydrocarbon diluent as drier compositions and in drying oil compositions. The drier compositions can contain a high cobalt content, e.g., 12% cobalt by weight of the drier compositions. These salts have an amount of metal such that the sum of the stoichiometric amount of the metal and the excess corresponds to at least about 115% of the amount for neutralization of the acid by cobalt metal. The process used to make such salt reacts an excess of the metal with the acid in the presence of water and oxygen-containing gas for a time longer than required to neutralize the acid with metal. Then water is removed.

This application is a continuation of our copending patent application Ser. No. 566,761, filed July 21, 1966, and now abandoned.

This invention relates to drying oil compositions containing cobalt and to drier compositions containing basic cobalt salt of neoalkanoic acid and relates also to the process of the manufacture of such basic cobalt salt.

A paint is defined in "The Condensed Chemical Dictionary," Sixth edition, published in 1961 by Reinhold Publishing Corp., New York, N.Y. as "a liquid mixture which may be applied to surfaces to form a dry, thin, protective or decorative film." Some paints are referred to as enamels. Some enamels based on tall oil alkyds are referred to as short oil alkyd enamels, medium oil alkyd enamels or long oil alkyds.

That dictionary defines varnish as "an unpigmented oil-base paint composed of a solvent and either of two types of binders." One type of binder forms a film by oxidation or polymerization, such as drying oils alone or in combination with other materials such as natural or synthetic resins. The other type of binder forms films by evaporation of the solvent, such as shellac and alkyd varnishes. Some varnishes are formulated such that they are applied as hot spray. The temperature of the varnish is illustratively 150° F.

The term "drying oil composition" as used herein refers to pigmented paints containing drying oil and to varnishes containing drying oil, such as mentioned above.

As pointed out in the book entitled "Paint Technology Manuals, Part Two, Solvents, Oils, Resins and Driers," published in 1961 on behalf of Oil and Colour Chemists' Association by Chapman and Hall, Ltd., London, England, at page 31, paints containing drying oils mixed with certain pigments such as red lead, white lead and umber, dried faster than the oils not mixed with these pigments. This led to the development of the use in drying oil compositions of soluble metal compounds, that improved the drying rates of these oils, such as saturated naphthenate driers which are the metal salts of naphthenic acids. The principal metal salts have been the lead, cobalt and

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manganese salts. Instead of these metal salts of naphthenic acids, some driers have been offered as salts of octoic acid, nonoic acid and tall oil acid as indicated on page 31 of that book.

As pointed out on page 32 of the book, the primary function of a drier in paints and varnishes, i.e., drying oil compositions, is to accelerate the oxidation of the unsaturated oil and so speed up the drying of the paint film.

The book by the Oil and Colour Chemists' Association, mentioned above, refers to the nature of the organic acid radicals of the driers and to the metal compounds most commonly used in the manufacture of the driers. Cobalt sulfate is listed as the cobalt compound used and there is described a precipitation process for making cobalt naphthenate from this cobalt compound and sodium naphthenate obtained by reacting naphthenic acid with caustic soda aqueous solution. The reactions are presented on page 35 of the book, where it is indicated that the amount of cobalt sulfate is slightly less than the stoichiometric amount required to react with sodium naphthenate. Presumably the cobalt naphthenate is a neutral salt.

In the commercial process, according to this book, the cobalt naphthenate product is thinned with white spirit, i.e., mineral spirits which is a narrow-boiling-range fraction of petroleum with a boiling range between about 200° F. and about 300° F.

The conventional diluted drier composition contains 6% by weight of cobalt metal. More concentrated drier compositions have been prepared, but the viscosities of such compositions are too great for convenient use in the formulation of drying oil compositions.

The dictionary mentioned above defines driers as "chemical additives used to accelerate the drying period of paints, varnishes, printing inks and the like by catalyzing the oxidation of drying oils or synthetic resin varnishes, such as alkyds, which dry by air curing." Page 45 of the book by the Oil and Colour Chemists' Association, mentioned above, presents the percentage of metal introduced as metal salt of organic carboxylic acids, such as naphthenic acids, incorporated in various types of paints, varnishes and alkyds. These metals are cobalt, lead and manganese. In certain alkyds calcium metal as calcium salt is also present or is optionally present.

Lead naphthenate, as a commercial product, has been made to contain 24% by weight of lead metal, whereas cobalt and manganese naphthenates, as commercial drier compositions, contain 6% by weight of metal. The use of lead drier is such as to provide a substantially larger weight percentage of metal than the weight percentage of cobalt. However, the use of the drier composition of cobalt naphthenate with 6% by weight of cobalt and the lead naphthenate drier composition containing 24% by weight of lead metal has permitted easy formulation of drying oil compositions as paints, varnishes and alkyds because of this 4:1 ratio of metal content, i.e., lead to cobalt, permitting the use of their drier compositions in relative amounts that represent for both whole numbers in many cases.

It has been desirable to provide a cobalt salt containing a higher metal content than 6% by weight, but until recently none of the formulations developed provided a concentration, such as 12%, that is a multiple of 6%, would provide the advantage outlined above. Most of these were drier compositions containing substantially less than 12% by weight of cobalt. These cobalt drier compositions have been either neutral or slightly acidic.

One recently available cobalt drier composition has been examined and found to contain 12.01% by weight of cobalt. This cobalt drier composition contains a cobalt salt of neodecanoic acid and thus is designated 12% Co-

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balt Neodecanoate. This drier composition has an acid number of +5. It had a high measured Gardner viscosity of 0 at 25° C., which is convertible to a viscosity of 3.70 poises using the table on page 56 of the book entitled "Paint and Varnish Manual Formulation and Testing" by Philip L. Gordon and Ruth Gordon, published in 1955 by Interscience Publishers, Inc., New York, N.Y.

U.S. Pat. No. 2,409,678 of C. H. Hamblet describes and claims a process for the preparation of heavy metal salts of organic acids, such as naphthenic acid and long chain fatty acids. The process uses heavy metals. Lead, copper and zinc are among the heavy metals expressly mentioned. In the process an organic acid is converted to the corresponding metal salt by direct contact with the metal in the presence of oxygen. The process of the patent is concerned with the prevention of degradation of the organic acid during the reaction in the presence of anti-oxidant. That patent refers to two other patent applications which have become U.S. Pats. Nos. 2,395,307 and 2,416,074, filed by A. G. Weber and C. H. Hamblet. U.S. 2,395,307 reacts the heavy metal with the heated organic acid while in contact with oxygen, whereas U.S. 2,416,074 uses an ester of the organic acid in the presence of water to react with the heavy metal while in contact with oxygen. These processes are substitutes for prior methods of forming the metal salts of the organic carboxylic acids. Cobalt is a heavy metal and thus would be suggested for such reaction. U.S. 2,395,307 teaches the desirability of introducing water during the course of the reaction.

U.S. Pat. No. 2,528,803, granted to G. G. Unkefer discloses a process utilizing the reaction of a heavy metal with an organic carboxylic acid, such as naphthenic acid and 2-ethylhexoic acid, in which the reaction is accelerated by the presence of two types of materials, one of which is a low molecular weight organic carboxylic acid, such as acetic acid. The other material is an alcohol. The process does not require the presence of water but it may be present. It is stated that the advantage of not adding water is that drying of the product is not necessary. It is understandable that the acetic acid would increase the rate of reaction because it is a stronger acid than the higher molecular weight acids, such as naphthenic acid and 2-ethylhexoic acid.

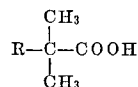
Other U.S. patents have disclosed the process of making heavy metal salts of organic carboxylic acids by reacting a heavy metal with an organic carboxylic acid. One patent is U.S. 2,584,041 granted to M. Nowak and A. Fischer. At a temperature above 100° F., the heavy metal is reacted with an organic acid, such as naphthenic acid and 2-ethylhexoic acid. Some of the examples describe the preparation of cobalt naphthenate drier composition containing, after dilution with mineral spirits, 6% by weight of cobalt. Another example describes the preparation of a 6% cobalt salt, after suitable dilution with mineral spirits, in which the organic acid used was a mixture of tall oil acids and naphthenic acid.

The various patents mentioned above refer to the metal salts as metal naphthenate except for U.S. 2,584,041 which describes the preparation of some lead salts as basic lead salts. Specifically Example 18 describes the preparation of lead naphthenate, whereas the Example 19 describes the preparation of basic lead naphthenate. Both are indicated as being useful as drier compositions. The preparation of basic lead naphthenate is not surprising in view of the fact that lead is an amphoteric chemical element. As explained earlier, salts of the organic carboxylic acid and of other metals are prepared as neutral salts. Some are somewhat acidic due to the use of the organic acid in an amount slightly greater than stoichiometric.

A new type of organic carboxylic acid became available as a new product a few years ago. This product is neodecanoic acid and the available material as a new product is indicated by an announcement dated January 1960, by Enjay Company, Inc. under bulletin MD-238. Neo-

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decanoic acid is described as a branch-chain aliphatic monobasic acid derived from petroleum. This organic carboxylic acid has two methyl groups attached to the carbon atom immediately adjacent to the carboxyl group so that molecular structure of neodecanoic acid is represented by the formula:



where R represents various branched alkyl groups containing 6 carbon atoms. In this formula the carbon adjacent to the carboxyl group is a diamond carbon atom because it has four carbon atoms attached to it. The generic term for such molecular structure is neoalkanoic acid. In view of the branching that occurs in the R group the compounds defined by the term neodecanoic acid are neoalkanoic acids containing branching beyond the diamond carbon atom. Neodecanoic acid as a commercial product contains a small amount of branch-chain aliphatic monobasic acids containing 9 atoms and 11 carbon atoms with this neoalkanoic acid structure.

Neodecanoic acid has been recommended in that bulletin for possible use in the form of cobalt, manganese and lead soaps, as driers. This neodecanoic acid has been used to prepare the cobalt neodecanoate drier composition containing a theoretical 6% by weight of cobalt. The preparation of this drier has been described by Enjay bulletin ECL 6605 1448 as follows:

Neodecanoic acid (206.4 gm.; 1.2 mole) is reacted with 1140 ml. of 1 N sodium hydroxide in a 4-liter beaker at 60° C. The solution is then diluted to 1600 ml. with distilled water. Baker Reagent cobalt chloride hexahydrate (142.8 gm.; 0.6 mole) in 1 liter of warm (50° C.) distilled water is added slowly with stirring to the sodium salt solution. A deep blue drier forms immediately and, after addition of all the cobalt chloride solution, 260 gm. of ISOPAR K (an odorless mineral spirits made synthetically and constituting a mixture of isoparaffin hydrocarbons that are highly branched with a boiling range between about 345 and 410° F.) is added to take up the viscous blue layer. After 20 minutes stirring, the layers are separated and the organic layer washed with warm water (50° C.) to remove water-soluble salts. The deep blue organic layer is then transferred to a 2-liter flask and distilled to remove excess solvent and water (collected in Barrett trap). Solvent is removed until the theoretical weight of 6% cobalt is reached, and the solution is filtered. A small quantity of neodecanoic acid (10 gm.) is added at the end to stabilize the solution against sludging.

U.S. Pat. No. 2,116,321 discloses an ink drier embodying a basic cobalt salt of naphthenic acid of high, e.g., 18% by weight, cobalt metal content. These salts are solids rather than liquids and are mentioned as being substantially insoluble in oil. The procedure, by which this basic cobalt salt of naphthenic acid is made, is described in that patent. An aqueous solution of cobalt sulfate is added to an aqueous solution of sodium naphthenate, obtained from caustic and naphthenic acid and containing an excess of caustic. A blue precipitate is formed.

In U.S. Pat. No. 2,368,560 this kind of basic salt, referred to as hydroxy metal soap, is illustrated by such copper soap which is made by the double decomposition process of U.S. Pat. No. 2,116,321. Instead of powder the process of the latter patent provides the salt in colloidal form, dispersed in petroleum distillate. Thus the basic cobalt salt of these patents is not capable of forming a solution in mineral spirits or in the drying oil compositions to which drier compositions are added in the formulation of paints, varnishes, etc.

U.S. Pat. No. 2,955,949 discloses a process of making trialkyl acetic acids, i.e., neoalkanoic acids such as neodecanoic acid and paint driers of their lead, cobalt and

manganese salts. It discloses a column 5, lines 50-54, that such acids "readily form basic salts" with cobalt, manganese and lead. The only description of a process of making a cobalt salt of trialkyl acetic acids is the precipitation method. Apparently this is the process used to make "basic" cobalt salt, i.e., make a salt that doesn't require excess acid. However, Enjay Co., Inc., an affiliate of the assignee of that patent, has described in the more recent report mentioned above the preparation of oil-soluble cobalt neodecanoate in which the stoichiometric double decomposition action is followed by the addition of a small amount of neodecanoic acid to provide a composition of the salt in the mineral spirits that is stabilized by the acid against sludging.

Some of the objects of the present invention are to provide a cobalt drier composition:

(a) In which a cobalt salt is oil-soluble and contains cobalt and neodecanoate groups in proportions such as to reduce the cost of manufacture as compared with neutral or acidic salt of those groups;

(b) That contains oil-soluble cobalt neodecanoate salt in a concentration to provide a cobalt metal content of greater than 6% by weight and preferably of about 12% by weight in which the cobalt salt of neodecanoic acid is such that the composition has a suitably low viscosity; and

(c) In which the cobalt salt is oil-soluble and the drier composition contains about 12% by weight cobalt metal content to reduce shipping costs but also has a satisfactorily low viscosity to provide ready dissolution in the making of paint formulations and the like due to the low viscosity of the drier composition.

Another object of this invention is to provide drying oil compositions containing cobalt drier in an oil-soluble form as a salt in which the organic acid content is less on a stoichiometric basis than in oil-soluble salts used heretofore.

It is a further object of the invention to provide a process for the manufacture of drier compositions and drying oil compositions of the types stated above in the other objects.

These and other objects of the invention will be apparent to one of ordinary skill in the art from the following description of the invention.

The present invention as a process reacts cobalt metal with neodecanoic acid, as the relatively pure material or as the commercial product that contains minor amounts of the C_9 and C_{11} trialkyl acetic acids, in the presence of air or other oxygen-containing gas and in the presence of water, at an elevated temperature, such as between about 140° F. and about 280° F., preferably between about 170° F. and about 190° F. while mixing the acid and granular cobalt metal. The mixture contains mineral spirits or similar material that dilutes the acid. The mixture preferably uses a small amount of acetic acid, which can be added with the water as a dilute acetic acid aqueous solution, to accelerate the rate of reaction between the metal and the neodecanoic acid. This mixing of the ingredients can be carried out under conditions where there is some loss of volatile material, but this loss can be overcome by periodic addition, if desired, of mineral spirits or other suitable solvent.

The process of the invention as described in the preceding paragraph is a conventional process. The difference in the process is that the former uses relative amounts of the neodecanoic acid and the metal and a sufficient time and temperature of reaction that at least 105% preferably at least 115% of the neodecanoic acid is neutralized by reaction with the cobalt metal. This degree of neutralization of the acid is a reaction that actually prepares a basic cobalt neodecanoate in which the term "basic" as used in this specification's description of the invention and in the claims refers to the alkalinity or basicity of the salt. This degree of neutralization for a drier composition of the invention containing the salt in a concentration

to provide 12% by weight of cobalt metal can be expressed by a negative value for acid number, and such values of acid number can range between about -30 and about -70, preferably between about -30 and about -60. The term "acid number" has the conventional meaning, namely, the milligrams of potassium hydroxide required to neutralize one gram of a sample of such material having the stated acid number. The percent of neodecanoic acid neutralized is a term used to express alternatively the basicity. It expresses also the relative amounts of cobalt metal and of the neodecanoate group combined in the oil-soluble product having this substantial degree of basicity.

In carrying out the process the starting mixture for the reaction may be added to a reaction vessel having a reflux condenser to reduce substantial loss of volatile materials during the reaction. The mixing can be provided by mechanical means, but sufficient air or other oxygen-containing gas must be introduced into the mixture of reactants because oxygen participates in the overall reaction. The air may be introduced in a manner to provide the intimate mixing of the ingredients.

During the reaction the liquid material is being intimately mixed with the metal. This mixture during the reaction is at an elevated temperature as mentioned above. Particularly if the mixture is cooled to room temperature after the reaction has proceeded to the extent that the percentage of acid neutralized that is attained in carrying out the process of the present invention, the reaction mixture is non-homogeneous. However, this reaction product, after heating to a high enough temperature for removal of water, becomes a liquid that remains homogeneous even when cooled to room temperature. The percent acid neutralized of the reaction product after water removal is at least 105 and preferably much higher.

The minimum basicity, expressed as 105% of neodecanoic acid neutralized, is stated above. The maximum percentage of acid neutralized by cobalt is determined by the amount of basicity to be provided without losing the requisite oil solubility. This basic cobalt neodecanoic salt has been made by the process with as high a basicity as 146% neodecanoic acid neutralized. To provide a safety factor i.e. to avoid the formation of a product that is not oil soluble, it is preferred that the basicity be a maximum of about 135% neodecanoic acid neutralized. These salts are such that by suitable dilution with the mineral spirits or other solvents, particularly hydrocarbon solvents, there can be provided a drier composition containing 12% by weight of cobalt. This composition has a low viscosity and thus permits ready mixing of it into drying oil compositions.

The reaction product obtained by the process of this invention contains a stoichiometric excess of cobalt relative to the organic acid, i.e., contains more cobalt than would be present in a neutral cobaltous salt of this acid. This excess is expressed by the minimum value of 105% neodecanoic acid neutralized that is expressed above. This value can be expressed as 5% basicity for the product which is termed basic cobalt neodecanoate. It is preferred that the percent of neodecanoic acid neutralized in the product of the process be at least 115, i.e., it is preferred that the product be at least 15% basic. In view of the fact that the higher the percent basicity, the greater the saving and cost of starting materials due to the lessened content of neodecanoic acid radical, it is most desirable to provide as the product of the invention the basic cobalt neodecanoate in which the neodecanoic acid is at least 130% neutralized by cobalt. Of course, there is the upper limit, beyond which the basic cobalt neodecanoate has a composition such that it is not soluble in mineral spirits or other similar liquid ingredients for drying oil compositions and is not soluble in the drying oil compositions.

Although neutral or acidic cobalt salts of organic acids as drier compositions in which cobalt metal content is

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12% by weight of the drier have been known, the possibility of preparing a soluble basic cobalt salt and having a basicity of at least 5% was not believed to be possible, especially with one with such high cobalt metal content for the drier composition.

The drier composition of the invention preferably contemplates compositions in which the degree of basicity is that referred to above. In this preferred drier composition the cobalt metal content is 12% by weight. Even with this high cobalt content in the preferred drier composition, the degree of basicity is preferably at least 30%. These drier compositions with the higher degree of basicity and the higher cobalt metal content expressed as the preferred embodiment provide the numerous advantages already described.

As is seen later, the drier compositions of the present invention can be used to provide the same cobalt metal content for drying oil compositions as the cobalt metal content heretofore included in such compositions by the use of neutral or acidic cobalt salts of other organic acids, such as naphthenic acid and 2-ethylhexoic acid. Of course, the drier compositions can be mixed, in any conventional concentration of neutral or acidic cobalt salt, with manganese drier composition, lead drier composition, zirconyl drier composition, or combinations of these. The zirconyl salt is a substitute for lead drier in numerous formulations of drying oil compositions.

These drier compositions of salts of other metals can be incorporated in the drier composition of basic cobalt neodecanoate of this invention by co-manufacture of such metal salts as neodecanoates in the case of those metals that form the desired salt by reaction of the metal as such with neodecanoic acid. In accordance with this requirement, zirconyl salt would not be co-manufactured because it is prepared by a different type of a reaction.

The lead or manganese salt of neodecanoic acid also can be separately prepared and then mixed with the basic cobalt salt of drier composition in a desired ratio of the two metals or can be separately supplied for incorporation in the drying oil composition.

The following examples illustrate the process of the invention and the drier composition containing basic cobalt neodecanoate, especially as a composition with a 12% cobalt metal content. One example illustrates drying oil compositions containing this basic cobalt neodecanoate in a couple of formulations. There are presented comparative tests of such formulations using 6% cobalt neodecanoate having an acid number of 6 and with commercial 6% cobalt naphthenate. The drying times are compared using only cobalt and using cobalt with lead neodecanoate or lead naphthenate as seen below.

EXAMPLE I

A 600-gram content of neodecanoic acid was diluted with mineral spirits. A small amount of water and a few drops of acetic acid were added. The mixture was stirred into a vessel containing an excess of granular cobalt. This mixture was blown with air and reacted at 90° F. to 172° F., the latter being the highest temperature reached during the course of the reaction. Samples of the mixture were taken periodically and the organic phase of a sample was titrated to determine its acid number. When a sample by its acid number indicated the completion of the reaction in a stoichiometric sense by having an acid number of zero, the introduction of air and the mixing were ceased. The batch was allowed to cool overnight.

The next day the organic phase was sampled and found to be a product having 106% of the neodecanoic acid neutralization, i.e., 6% basic. The rest of the organic phase was reheated to a temperature sufficient to remove water and some of the mineral spirits. It was found that the dehydrated product contained 12.05% cobalt metal and this product contained 118% neodecanoic acid neutralized, i.e., was 18% basic. In spite of this high cobalt content and the high degree of basicity which was

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unexpected in view of the reaction being stopped when the acid number was zero, it was also surprising to note that this dehydrated product was a thin fluid, i.e., a fluid having a low viscosity. Surprisingly this product is soluble in mineral spirits and conventional drying oil compositions.

This product has the economic advantages due to its lower content of relatively expensive organic acid and its lowered shipping and handling costs due to its higher cobalt content that reduces the volume of cobalt product shipped to provide a specific content of drier for a given quantity of drying oil composition to be manufactured.

EXAMPLE II

The reaction of neodecanoic acid with excess of granular cobalt in the presence of mineral spirits as a diluent, with water and acetic acid as catalyst and with the mixture being blown with air at an elevated temperature, was performed with samples being taken at regular intervals and titrated for acid number. The reaction proceeded to the extent that it was indicated by the acid number that the acid was more than 100% neutralized. However, the degree of basicity appeared to reach a maximum value of 10% even though the reaction was conducted for a prolonged period of time. The samples solidified when permitted to cool. Although the acid number of the various samples indicated that the reaction process apparently had reached a static condition of a certain basicity, as mentioned above, it was found that such samples when heated to remove water became homogeneous fluids having a basicity appreciably higher than the corresponding sample before water removal. Furthermore, it was discovered that instead of the basicity remaining constant from one sample to a later sample, the degree of basicity had increased with the duration of the reaction.

EXAMPLE III

A further study of the reaction under conditions similar to the reaction performed in Example II provided a dehydrated fluid product containing 12% by weight of cobalt metal basic cobalt neodecanoate having a basicity of 35%. Such product was obtained after eight hours of reaction. Periodic samples taken earlier in the course of the reaction and titrated directly, i.e., determined for acid number without water removal, would have indicated that the basicity was remaining constant at a value of 10% over a period of the last four hours of the period during which the course of the reaction was followed.

EXAMPLE IV

A reaction flask was charged with 750 grams of a technical grade of neodecanoic acid obtained from Enjay Company, Inc. This acid had an acid number of 318. This acid was diluted with 750 grams of mineral spirits. To this mixture, 200 grams of 2.5% acetic acid aqueous solution were added. This batch of ingredients was heated to 180° F. Cobalt granules in the amount of 196 grams were added to this batch that had been heated to 180° F. while the batch was being stirred. Air was bubbled into the contents of the reaction flask. Hourly samples of the reaction mixture were taken. The cobalt content of a sample was determined by the method designated ASTM-D-2373. The acid number, positive or negative, was determined by the method described later. From these two values the percent of neodecanoic acid neutralized by the cobalt was calculated, as explained later.

The acid number method and the determination of the percent acid neutralized as well as the cobalt content determination for the other examples were determined in the same manner.

The samples were non-homogeneous, as discussed earlier, and only a portion of the sample was utilized to determine the percent acid neutralized by cobalt. Another portion of each was heated to remove water. The dry sample was analyzed for cobalt content and acid number to determine its percent of acid neutralized. The following tabulation presents the results of the present neutralized

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for each sample, prior to water removal and designated a wet sample, as compared with a sample after water removal and designated a dry sample. The discrepancies and variations are believed to be due to the lack of homogeneity.

Sample number	Neodecanoic acid neutralized, percent	
	Wet sample	Dry sample
1.....	44	44
2.....	71	70
3.....	92	94
4.....	103	114
5.....	117	116
6.....	116	120
7.....	121	122
8.....	124	126
9.....	109	111
10.....	136	129
12.....	122	146

When analysis of a sample after heating for dehydration showed the product contained more than 135% of the acid had been neutralized, the mixing of the reactants was stopped. The mixture separated into two phases. The upper phase was removed and vacuum stripped for removal of water and excess solvent. This dehydrated product was filtered. Mineral spirits was added to dilute the concentration of cobalt salt so that the final product contained 12% cobalt by weight. This product weighed 1400 grams and, more important, had a viscosity of A Gardner at 25° C. According to the conversion tabulation in the book by P. L. Gordon and Ruth Gordon mentioned above, the A Gardner viscosity represents a viscosity of 0.5 poise.

EXAMPLE V

Cobalt metal granules were reacted with neodecanoic acid diluted with mineral spirits in the presence of water and acetic acid with mixing of the reactants and with bubbling of air through the mixture described in earlier examples. Duplicate samples were taken periodically during the course of the reaction. One of the duplicate samples was allowed to settle and the upper layer was analyzed for acid number and cobalt metal content to determine the percent of neodecanoic acid neutralized. The other sample of the duplicate set was heated to 300° F. for dehydration and then analyzed for acid number and cobalt content. The following are the values of percent neutralization obtained for the samples.

Reaction, hours	Neodecanoic acid neutralized, percent	
	Settled sample	Dehydrated sample
1.....	46	46
2.....	76	76
3.....	65	93
4.....	109	113
5.....	108	112
6.....	107	112
7.....	111	115
8.....	111	115
9.....	120	135

EXAMPLE VI

The following data show the percent acid neutralized for the reaction performed in two different runs.

Sample number	Neodecanoic acid neutralized, percent	
	1st run	2nd run
1.....	63	44
2.....	78	66
3.....	89	66
4.....	99	79
5.....	107	86
6.....	108	92
7 Process terminated.....	108	108
Product.....	113	116

All of these numbered samples had the percent of neutralization determined without any water removal. The percent of neutralization of product represents the value

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determined for the product after it had been dehydrated.

It is to be noted that the product designated as 1st run had the neodecanoic acid only 113% neutralized by cobalt but the second one had the neodecanoic acid 116% neutralized cobalt. The latter value is within the preferred range of percent neutralized. Five other runs provided percent of neutralization of 123, 117, 116, 108 and 119% for the dehydrated product. However, as seen earlier, drier composition containing basic cobalt neodecanoic having 146% neodecanoic acid neutralized by cobalt and with a cobalt content by weight of about 12% in the drier composition has been obtained.

EXAMPLE VII

This example illustrates the use of the drier composition of the invention in drying oil compositions of the present invention and provides a comparison with conventional cobalt salts heretofore available.

Enamels having the following compositions by weight were used.

Enamel Ingredients	Enamel compositions percent by weight	
	Long oil soya alkyd	Medium oil linseed alkyd
25 Titanium dioxide.....	30.12	30.95
Zinc oxide.....	2.57
Beckosol P-296-70.....	48.99
Nuosperse 657.....	0.35
Varsol solvent.....	17.97
Beckosol P-670-55.....	52.22
VM & P naphtha.....	16.83
30 Total.....	100.00	100.00

The Beckosol products shown above are the alkyd resins. Nuosperse is a dispersing agent. Varsol is a well-known type of hydrocarbon solvent.

To these enamels were added cobalt driers of different types, alone and with lead drier. The quantity of drier and type used is shown below along with the results of set-to-touch drying times, as determined with the finger, for the final formulations. The 6% cobalt neodecanoate used for comparison with the basic cobalt salt of the invention had an acid number of 6, whereas the basic cobalt neodecanoate drier composition of the present invention contained 12% cobalt and had a base number of 40, i.e., an acid number of —40.

Drier type added	Quantity used †	Drying time, minutes	
		Long oil alkyd	Medium oil alkyd
50 6% Co neodecanoate.....	0.05% Co.....	131	27
12% Co neodecanoate (basic).....	0.05% Co.....	133	29
6% Co naphthenate.....	0.05% Co.....	161	34
6% Co neodecanoate plus.....	0.05% Co plus.....
Pb neodecanoate.....	0.5% Pb.....	126	19
12% Co neodecanoate (basic).....	do.....	127	18
55 Plus Pb neodecanoate.....
6% Co naphthenate plus.....	do.....	133	29
Pb naphthenate.....

† Based on resin solids.

The foregoing data show that there is no appreciable difference in effectiveness as regards drying time between the two cobalt neodecanoates and shows that both are better than cobalt naphthenate as drier.

The erratic values of percent of neutralization obtained by the analysis of samples taken during the course of the reaction has been demonstrated by earlier examples. It has been determined that this is due to the fact that in the reaction mixture this basic cobalt neodecanoate forms a gel-like mass in the presence of water. Thus it is difficult to obtain representative samples of the product at the later stages of the reaction.

The Enjay bulletin that describes the preparation of 6% cobalt neodecanoate is mentioned above, having a plus value for acid number. That description indicates that 585 lbs. of neodecanoic acid would be treated with 100 lbs. of cobalt to produce this cobalt salt that is slightly

acidic. The present invention provides a reaction in which the ingredients are present in a different proportion such that the reaction product is that produced by reaction of 100 lbs. of cobalt with as small amount as 433 lbs. of neodecanoic acid. In view of the fact that 1 lb. of the basic cobalt neodecanoate drier composition of the present invention containing 12% cobalt can be used in place of 2 lbs. of neutral or acidic 6% cobalt neodecanoate drier composition or neutral or acidic 6% cobalt other salt drier composition, there is thus a saving of shipping cost and materials handling, as well a reduced use of relatively expensive organic carboxylic acid to form a cobalt salt for use as a drier.

Throughout this description reference has been made to acid number, positive or negative. The values have been determined by a slight modification of the method developed by E. W. Diener and S. Werthan reported in the Proceedings of the American Society for Testing Materials, volume 30, Part 2 (1930), pp. 924-927. In the modified method, a sample of about 5 grams is placed in a beaker. The sample is weighed to the nearest centigram. A 5-ml. quantity of standardized organic carboxylic acid solution in mineral spirits (having a titer value between 11 ml. and 12 ml. of 1 N sodium hydroxide solution) is added to the beaker, unless the sample is known to be acidic. Thereafter 25 ml. of chloroform, 50 ml. of anhydrous methanol and 25 ml. of potassium oxalate solution are added. This potassium oxalate solution is a saturated solution obtained by adding 700 grams of potassium oxalate to 2 liters of distilled water with heating of the mixture until the salt is dissolved followed by cooling.

The mixture of sample, carboxylic acid solution, methanol and potassium oxalate aqueous solution is heated with stirring to the boiling point and then removed from the heat. After adding 1 ml. of a 1% alcohol solution of phenolphthalein, the solution is titrated with standardized 1 N sodium hydroxide aqueous solution.

The acid number, mg. of KOH per gram of sample, is calculated as follows:

$$\text{Acid No.} = \frac{(BN - A)56.1}{S}$$

where

B=ml. of standard NaOH consumed

N=normality of NaOH consumed

A=ml. of N NaOH equivalent to carboxylic acid addition

S=sample weight in grams.

A negative acidity is indicative of a basic salt.

The following illustrates the calculation, from cobalt content and from acid number of a drier composition of the invention, the percent of neodecanoic acid neutralized by cobalt. Let us assume that a dehydrated sample at the end of the reaction of the process has an acid number of -50 and contains 10% cobalt metal by weight. One hundred grams of sample contains C equivalents of cobalt, or

$$C = \frac{10 \times 2}{58.9} = 0.339$$

The quantity of excess or basic cobalt is expressed as 50 milligrams (as KOH) per gram of sample. This is expressed as equivalents of cobalt per 100 grams of sample as follows:

$$\frac{0.05 \times 100}{56.1} = 0.089$$

The equivalents of acid which have been neutralized are therefore

$$N = 0.339 - 0.089 = 0.250$$

The percentage of acid neutralized by cobalt is

$$\frac{C}{N} \times 100 = \frac{0.339}{0.250} \times 100 = 135.5\%$$

The basicity is

$$\left(\frac{C}{N} - 1\right) \times 100 = 35.5\%$$

- 5 When the product is concentrated to 12% Co by removal of solvent, the acid number is increased to -60.

$$-50 \times \frac{12}{10} = -60$$

- 10 Since the metal salt is otherwise unchanged, the basicity remains at 35.5%. This basicity percentage is an expression of the percentage, by weight or by equivalents, of cobalt in the basic cobalt salt that is in excess of the cobalt content of a neutral cobalt salt of the organic acid, i.e., cobaltous salt of the organic acid in which one-half of the formula weight of cobalt is combined with the formula weight of the anion of the organic monocarboxylic acid.

A sample of the 12% basic cobalt neodecanoate drier composition of the present invention is compared below with a sample of a recently obtained 12% acidic cobalt neodecanoate.

These contained 12.17 and 12.01% cobalt metal by weight, respectively. Both had a royal blue color. The basic cobalt neodecanoate drier of the invention had an acid number of -37, a non-volatile material content of 66% with an A-2 Gardner viscosity at 25° C. (0.220 poise) whereas the acidic cobalt salt had an acid number of +5, a non-volatile material content of 75% by weight and an 0 Gardner at 25° C. (3.70 poises).

The Enjay bulletin of January 1960, on neodecanoic acid and designated MD-238 refers to this acid as Neo-Decanoic Acid. It indicates the following values for a typical inspection.

Acid No., mg. KOH/g. -----	311.5.
Theoretical Acid No. -----	326.
Saponification No., mg. KOH/g. -----	335.9.
Color, Gardner -----	1.
Refractive Index, N ₃₈ /D -----	1.4388.
Viscosity at 100° F., Saybolt Sec. ----	84.8.
Appearance -----	Colorless liquid.
Density 20/4 -----	0.9110.
Distillation ¹ , ° C.: -----	
I.B.P. -----	79/10 mm.
5% -----	112.
50% -----	130.
95% -----	138.
Dry Point -----	145.

¹ In apparatus similar to ASTM D1160-57T.

The foregoing description and examples provide a sufficient disclosure of the various embodiments of the present invention. Various modifications will be obvious to one of ordinary skill in the art from the teaching of the invention that is presented above. The example are merely illustrative of the invention which is limited only by the claims that follow.

We claim:

- 60 1. A process of preparing a drying oil soluble composition that contains about 12% cobalt as a product from the reaction of cobalt metal and neodecanoic acid and that remains homogeneous even when cooled to room temperature which consists essentially of:
- 65 (1) mixing particles of cobalt metal, neodecanoic acid, water and mineral spirits as a diluent for the neodecanoic acid, said cobalt metal being present in an amount that is at least 115% of the stoichiometric amount that would be present in neutral cobaltous neodecanoate obtainable from all of said neodecanoic acid;
- 70 (2) reacting the components of said mixture while said mixture is maintained at an elevated temperature between about 140° F. and about 280° F. while blowing the mixture with air for a period of time
- 75

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to form neutral cobaltous neodeconate from said neodecanoic acid and a part of said cobalt;

(3) then reacting the neutral cobaltous neodecanoate with remaining cobalt now in the mixture while maintaining said elevated temperature and while blowing the mixture with air for a further period of time sufficient to form a reaction product that has a minimum basicity of at least 15% and a maximum basicity of about 46%;

(4) then heating the admixture of reaction product, water, diluent, and any unreacted cobalt metal to remove by evaporation and water content thereof, said heating being at a sufficiently elevated temperature for said evaporation, to provide a composition that contains said product from the reaction of said cobalt metal and said neodecanoic acid and with said minimum basicity of 15% and maximum basicity of about 46%, that is dehydrated, and that has said solubility in said oil and has said homogeneity at room temperature; and

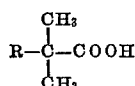
(5) adjusting the mineral spirits content to the extent necessary to provide said drying oil soluble composition containing about 12% cobalt, said basicity being based on a determination of said value for the dehydrated product.

2. The process of claim 1 wherein the reaction of cobalt metal particles and neodecanoic acid is carried out in the presence of a catalytic amount of acetic acid in addition to the water.

3. The process of claim 2 wherein the elevated temperature is between about 170° F. and 190° F.

4. The process of claim 3 wherein said further period of time of maintenance is such as to provide a reaction 35%.

to form a product that has a maximum basicity of about 5. The process of claim 4 wherein the neodecanoic acid is a technical grade in which in addition to neodecanoic acid having the formula:



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where R represents various branched alkyl groups containing six carbon atoms, such acid contains minor percentages of similar trialkyl acetic acids containing 9 and 11 carbon atoms, the temperature of reaction is 180° F., and the acetic acid and water were present by the use of a 2.5% by weight acetic acid aqueous solution, wherein, on weight basis, the initial mixture contains 750 parts each of the neodecanoic acid and mineral spirits, 196 parts of cobalt granules, 200 parts of said acetic acid solution, and wherein the total reaction is carried out for 12 hours followed by cooling with separation into layers and with separation of the upper phase containing the cobalt neodecanoate and treatment of that phase for the dehydration followed by the adjustment of mineral spirits content.

6. A composition prepared by the process of claim 1.

7. A composition prepared by the process of claim 2.

8. A composition prepared by the process of claim 3.

9. A composition prepared by the process by claim 4.

10. A composition prepared by the process of claim 5.

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JOAN B. EVANS, Primary Examiner

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106—264; 260—414