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PROCESS FOR STABLY DISPERSING METAL COMPOUNDS

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This invention relates to a process for the preparation of intermediates utilized in preparing stable dispersions for use as additives for lubricating oils and the like. More particularly, but not by way of limitation, this invention relates to a method of preparing alcohol soluble metal alkoxides and/or alcohol soluble carbonates of such metal alkoxides. In another of its aspects, the invention relates to a process for dispersing basic metal compounds, including metallic carbonates, derived from said metal alkoxides and the carbonates thereof in a nonvolatile carrier.

Dispersions containing certain oil-insoluble metal compounds which are dispersed by an oil-soluble dispersing or peptizing agent in a nonvolatile carrier material have recently acquired considerable importance as additives in lubricating oils. Such dispersions have also been highly useful as additives to other materials where the problem of suspending insoluble waste materials formed in the utilization of the material and also the problem of corrosion inhibition are met. For example, in lubricating oils of the heavy-duty detergent type, such as those used in diesel and similar internal combustion engines, at least two desiderata must be met by such oils. If a high degree of engine cleanliness is to be maintained, the oil must be capable of neutralizing acidic lacquer precursors which are formed by either oil oxidation, or by interaction of the oil with certain sulfur acids produced from fuel combustion, or by both of these conditions. Secondarily, the oil must possess the power to disperse such insoluble material as is formed by fuel combustion or oil oxidization in order that the abrasive and corrosive effect of said insolubles shall be minimized.

It is particularly desirable that lubricating oil compositions which are utilized in marine diesel engines have a high degree of basicity. The requirement of high basicity stems from the use of fuels in such engines which are characterized by high sulfur content which, in turn, means a larger amount of acidic combustion products are produced. For the purpose of dispersing or suspending the insoluble materials, such as sludge, formed in the use of such lubricating oils and the like, it is necessary to also add to the oil some composition which effectively peptizes or disperses insolubles, thereby retaining them in suspension in the lubricant.

The present invention provides a process for preparing certain valuable additives for use in internal combustion engine lubricating compositions, which additives are characterized by a high basicity and include an oil-soluble dispersing agent which functions to effectively disperse or peptize such insolubles are formed by fuel combustion, oil oxidization or similar conditions obtaining during the utilization of said composition. The additives are prepared in the form of highly stable dispersions of metal hydroxides or metal carbonates in a nonvolatile carrier. The substantial quantity of basic metal compounds which are present in such dispersions effectively combats the deleterious effect of acidic oxidization products, while the dispersing agent employed effectively prevents the precipitation or accumulation of sludge and insoluble material.

In addition, the present invention provides a means of preparing compositions which contain large amounts of dispersed cations. Such compositions have a variety of

uses, as, for example, homogeneous catalyst systems, corrosion inhibitors, and particularly corrosion inhibitors for vanadium-containing fuels, and fuel additives in general.

The advantages of using a basic inorganic compound to react with undesirable acid components in fuel or lubricating oil are both obvious and well known. In other applications, such as homogeneous catalyst systems or corrosion inhibitors for vanadium-containing fuels, the basicity of the additive is usually of little concern. In these instances, the primary concern is the cation available from the additive. The inorganic dispersions of the present invention have a considerable advantage over the oil-soluble neutral salts in that they contain a much greater amount of metal per unit weight or volume. This allows lower treatment levels to be used which in turn results in considerable economies.

Although the great utility and advantageous results derived from the use of an additive dispersion of this general type have been previously recognized by us, and are referred to in our copending patent application Serial No. 15,031, filed March 31, 1960, now U. S. Pat. No. 3,150,089, the present invention resides in the discovery of a process which permits a substantial variation in the character and properties of such dispersions to be realized. Thus, although in the cited copending application we have referred to a number of the benefits which are derived from a lubricating oil additive comprising a dispersion of certain magnesium-containing inorganic compounds in a nonvolatile carrier material, by the process of the present invention it has become possible to easily and quickly prepare similar dispersions in which the metallic compound may be derived from a great variety of different metals according to the particular property of the dispersion which is most desired.

The process is especially useful in that it permits the excess metal content of the dispersions prepared thereby to be predicted with considerable accuracy. Moreover, the process may be practiced without the requirement of extreme process conditions of time, temperature and pressure. The starting materials utilized in the process are relatively inexpensive, and the particles of the metallic compounds suspended in the final dispersion are uniformly small as contrasted to previous types of dispersions containing various metallic compounds. This constitutes an advantageous features of the dispersions prepared by the present invention in that the development of haze in the lubricating oil is prevented, and the particles of suspended metallic compounds do not reach a size sufficient to abrade the metal bearings with which the lubricating oil comes in contact. With respect to the small particle size of the dispersed metallic compounds, this characteristic of our dispersions is obtained without benefit of the time-consuming and complicated filtration processes which have frequently been required in preparing other types of lubricating oil additives which contain basic metallic compounds. Finally, the intermediates which yield the final metallic compounds suspended as the dispersoid in the dispersion additives as prepared in situ in a stable alcoholic solution and are therefore easily incorporated in the dispersion carrier material prior to final conversion by hydrolysis to the desired basic metal compounds.

Double decomposition reactions similar to those employed in the process of the present invention have been used previously in the preparation of lubricating oil additives of the alkyl-substituted metal phenolate types. In these particular reactions, a double decomposition reaction is used because the phenol is not strongly enough acidic to react with the less strongly basic metal oxides or hydroxides. The process of the present invention differs from that referred to. In the afore-mentioned process the dou-

ble decomposition reaction is used to produce phenates, which are essentially neutral and which do not contain excess metal as the desired product. In the present method, the double decomposition reaction is used to produce alkoxides, or alkoxide-carbonate complexes, as intermediates, which intermediates in turn are used to produce products containing excess basicity, or excess metal content, which is in contrast to the neutral phenates produced by the other process.

It is thus a major object of the present invention to provide an improved process for preparing beneficial additive compositions for lubricating oils, homogeneous catalyst systems, corrosion inhibitors, and the like.

It is also an object of the present invention to prepare a variety of metal alkoxide, or metal alkoxide-carbonate, intermediates, which intermediates may be very conveniently used for preparing a dispersion of basic metallic compounds in a nonvolatile carrier.

It is a particular object of the present invention to prepare a variety of metal alkoxide, or metal alkoxide-carbonate, intermediates which are derived from metals which are not reactive with alcohols, or metals which are only slightly reactive with alcohols, which intermediates may be very conveniently used for preparing a dispersion of basic metallic compounds in a nonvolatile carrier.

Another object of the invention is to provide a process by which an overbased dispersion of oil-insoluble basic metallic compounds in a nonvolatile carrier may be easily and inexpensively prepared.

A further object of the invention is to provide a process for preparing overbased dispersions having utility as additives for lubricating oil and the like, which dispersions are quite stable and are characterized in having relatively small and uniformly sized particles of metal hydroxides and/or carbonates dispersed therein.

A further object of the invention is to increase the number or variety of metallic hydroxides and/or carbonates which may be incorporated in an overbased dispersion for use in lubricating oils and the like.

Another object is to provide a method by which high basicity may be imparted to dispersions useful as lubricating oil additives, and to improve the control which may be maintained over the basicity attained.

These objects and advantages will become more clearly apparent, and additional objects and other superior aspects of the present invention will be understood, as the description of the invention proceeds.

Broadly stated, the present invention comprises a process which involves three reactions in proceeding from the raw materials utilized to the final overbased dispersions discussed above. In the first of these reactions, a sodium alkoxide is first prepared from the reaction between sodium and an alcohol, or by the reaction between sodium hydroxide and an alcohol. By virtue of the evolution of hydrogen, the first reaction is the simpler of the two. However, the sodium-alcohol reaction is more costly than the second method which employs sodium hydroxide and yields sodium alkoxide and water. The water which is produced is substantially removed from the reaction mixture by azeotropic distillation. The two preparations of the sodium alkoxide are expressed in the following equations:

(1) $2Na + 2ROH \rightarrow 2NaOR + H_2\uparrow$

(2) $NaOH + ROH \rightleftharpoons NaOR + H_2O$

Either reaction (1) or (2) may be utilized as the initial step in practicing the process of the present invention.

While the preceding step has used either metallic sodium or sodium hydroxide, it should be noted that any of the alkali metals or alkali metal oxides or hydroxides can be used. We prefer metallic sodium or sodium oxide or hydroxide because of general availability and price.

It should be noted that the azeotropic removal of the water, formed by the reaction of an alcohol with either sodium hydroxide or sodium oxide, is an important feature of this step. As shown above, the reaction of sodium hydroxide and an alcohol is an equilibrium reaction with the left hand reaction being dominant. Azeotropic removal of the water shifts the equilibrium to the right, thereby providing for a solution containing the metal alkoxide.

The second step in the process is a double decomposition or metathetical reaction which is accomplished by the addition of a metal salt to the alcoholic solution of the sodium alkoxide. In order for the double decomposition to occur leading to the formation of a metal alkoxide and a sodium salt, the metal salt which is added to the sodium alkoxide solution must be chosen so that the corresponding sodium salt which is produced is less soluble in the alcohol system than is the metal salt. The double decomposition reaction constituting the second step in the overall process of the invention may be expressed by the following equations:

(3) $nNaOR + MX_n \rightarrow M(OR)_n + nNaX$

Where

M=metal
X=anion
n=2, 3, 4, or 5, dependent upon the valency of the metal.

The insoluble sodium salt which is formed in this double decomposition reaction is removed by filtration or centrifugation. Such removal yields a stable, clear alcoholic solution of the desired metal alkoxide.

In some instances it may be desirable or necessary to carbonate the metal alkoxide in order to stabilize the alcoholic solution of such compounds. Whether or not such carbonation is required is dependent upon the requirements of the individual systems. The carbonation is achieved by passing carbon dioxide gas through the system, and the carbonation reaction can be expressed as follows:

(4)

$$M(OR)_n + xCO_2 \longrightarrow M(-O-\overset{\overset{O}{\|}}{C}-OR)_x(-OR)_{n-x}$$

Where

n is defined as indicated above, and
x is from 0.5 to 5, depending upon the valency of the metal and the solubility of the carbonate which is formed.

In some instances, carbonation of the metal alkoxide effectively increases the maximum metal content of the alcoholic solution and/or the ease of processing.

The third step in the overall process of preparing stable, overbased dispersions comprises that of incorporating the metal alkoxide or metal alkoxide-carbonate complex in a nonvolatile carrier by means of an oil-soluble dispersing agent, and then hydrolyzing the metal alkoxide to the corresponding metal hydroxide. In general, such incorporation is accomplished by first mixing a quantity of an oil-soluble dispersing agent, a hydrocarbon nonvolatile carrier and water and then heating such mixture to a predetermined temperature. The metal alkoxide or carbonate complex intermediate is then added to this mixture over a short period of time. Generally, the quantity of water incorporated in the mixture and the conditions of heat and time for adding the intermediate will be selected as necessary to effect as complete hydrolysis of the intermediates to their corresponding basic compounds as is possible. After the intermediate has been added to the dispersing agent-carrier-water mixture, the volatile solvents are removed by heating. Since in some cases it is more desirable to provide a metal carbonate in the dispersion than the corresponding metal hydroxide, it will, in such instances, be desirable to blow the dispersion with carbon dioxide in order to form the carbonate from the metal hydroxide.

In following the prescribed process to produce the final stable dispersion, the oil-insoluble, basic metallic com-

pounds which are suspended in the dispersion are of uniformly small particle size. The importance of using a soluble metal containing intermediate to prepare inorganic dispersions in oil is quite important. Such an intermediate permits the controlled precipitation of the inorganic phase as uniformly fine colloidal particles. The resulting colloidal dispersions are indefinitely stable under extreme conditions.

In the preceding description, for reason of convenience, we have used the terms "excess basicity" and "highly basic." It may be well to explain further what is meant. The process of the present invention is capable of preparing dispersions containing relatively large amounts of metal compounds. When the dispersoid metal compound is basic (e.g., calcium hydroxide), we can say that the dispersions are highly basic. However, the process is applicable to metals which are amphoteric. A dispersion containing a large amount of an amphoteric metal (e.g., aluminum) will not show a high basicity, even though the metal may be present as the hydroxide.

While our process is suitable for preparing a wide variety of alcohol soluble metal alkoxides or metal alkoxide-carbonate complexes, it is particularly suitable for preparing metal alkoxides or metal alkoxide-carbonate complexes wherein the metal or metal oxide is either non-reactive or only slightly reactive with an alcohol. In preparing such materials our process is superior to known processes. Examples of metals which are non-reactive or only slightly reactive with alcohols include: chromium, molybdenum, manganese, iron, cobalt, nickel, copper, zinc, cadmium, tin, lead, vanadium, zirconium, silver, mercury, arsenic, antimony, and bismuth.

Before setting forth a number of specific examples which illustrate our invention, it may be well to discuss, in general, the nature of the materials used and the more important process conditions of our invention.

The metal compound used in the double decomposition reaction must be one in which the corresponding sodium salt which is produced is less soluble in the alcohol system than is the metal salt (or compound). Suitable cations of the metal compounds include the metals of the following groups of the periodic table (according to Deming): I–B, II–A, II–B, III–A, III–B, IV–A, IV–B, V–A, V–B, VI–B, VII–B, and VIII. Particularly suitable cations, by reason of availability, economics, or non-reactivity (including slightly reactive) with alcohols, are the following: aluminum, silver, arsenic, barium, bismuth, calcium, cadmium, cobalt, chromium, copper, iron, mercury, magnesium, manganese, molybdenum, nickel, lead, antimony, strontium, tin, vanadium, zinc, and zirconium. Preferred cations, by reason of being either non-reactive or only slightly reactive with alcohols, are the following: silver, arsenic, bismuth, cadmium, cobalt, chromium, copper, iron, mercury, manganese, molybdenum, nickle, lead, antimony, tin, vanadium, zinc, and zirconium. Of the preferred cations, the following are particularly preferred, by reason of availability and economics: cadmium, cobalt, copper, chromium, manganese, nickel, and zinc.

Suitable anions of the metal salt include the following: halide, nitrate, sulfate, acetate, ammonium phosphate, bromate, carbonate, citrate, cyanide, dithionate, formate, iodate, nitrite, oxylate, phosphate, silicate, sulfide, sulfite, tartrate, aluminate, antimonate, arsenate, bismuthate, borate, chromate, manganate, molybdate, selenate, tungstate, uranate, and vanadate. Preferred anions of the metal salt include halide, nitrate, and sulfate.

Specific examples of suitable metal compounds include the following: aluminum chloride, barium chloride, cadmium chloride, calcium chloride, cobalt chloride, cupric chloride, magnesium chloride, manganese chloride, nickel chloride, strontium chloride, zinc chloride, tin chloride, chromic chloride, aluminum sulfate, barium nitrate, cadmium nitrate, calcium nitrate, cupric sulfate, magnesium sulfate, manganese sulfate, nickel sulfate, strontium sulfate, zinc sulfate, stannic sulfate and chromic sulfate.

The alcohols which are suitable in the process are those in which the metal alkoxide has an appreciable solubility. We have found suitable alcohols to be the following: aliphatic monohydric alcohols having from one to six carbon atoms, monoethers of ethylene glycol containing not more than eight carbon atoms, and monoethers of diethylene glycol containing not more than eight carbon atoms. Preferred glycol ethers are the monoethyl ether of ethylene glycol and the monomethyl ether of ethylene glycol. These materials are available commercially under the trademarks "Cellosolve" and "methyl Cellosolve." The monoethyl ether of diethylene glycol is available commercially under the trademark "Carbitol."

The monoethers of ethylene glycol are also known as alkoxy alkanols, and more specifically as alkoxy ethanols. These materials have the generic formula, $ROCH_2CH_2OH$, where R is a C_1 to C_6 hydrocarbon group. Similarly, the monoalkylether of diethylene glycol has the generic formula, $HOCH_2CH_2OCH_2CH_2OR$, where R is a C_1 to C_4 hydrocarbon group.

In conducting the azeotropic removal of water, it may be desirable to employ a known azeotroping agent, such as benzene or toluene. The use of such a material is necessary only when the alcohol employed does not form a "favorable" azeotrope with water. By "favorable" azeotrope is meant one which contains a relatively large amount of water. For example, the ethanol-water azeotrope is regarded as unfavorable due to the small amount of water present therein. The glycol ethers form an azeotrope with water and, for that reason, do not require an additional azeotroping agent. However, in some instances (such as convenience of operation) it may be desirable to add an additional azeotroping agent.

With respect to the types of nonvolative carriers which may be utilized in our process, a wide variety of materials have been found suitable for such usage. The principal requisites desired in the nonvolatile carrier are that it will dissolve the dispersing agents utilized in the process, and that such solutions will be relatively stable when the basic metallic compounds are peptized in the dispersion by the dispersing agent. Examples of such nonvolatile carriers which may be employed include mineral lubricating oil obtained by any of the conventional refining procedures; vegetable oils, such as corn oil, cottonseed oil, castor oil, etc.; animal oil, such as lard oil, sperm oil, etc.; and synthetic oils, such as polymers of propylene, polyoxyalkylenes, polyoxypropylene, dicarboxylic acid esters, such as esters of adipic and azelaic acids with alcohols such as butyl, 2-ethyl hexyl and dodecyl alcohols, and esters of acids of phosphorus, such as diethyl ester of decanephosphonic acid and tricresyl phosphate. The preferred nonvolatile carriers are liquid lubricating oils, either mineral or synethetic. If desired, the nonvolatile carriers may be diluted with a solvent to reduce the viscosity. Suitable solvents include petroleum naphtha or hydrocarbons, such as hexane, heptane, octane, benzene, toluene, or xylene.

A variety of oil-soluble dispersing agents may be used. Generic examples of suitable dispersing agents include the oil-soluble sulfonic acids, carboxylic acids, phosphorus sulfide-treated olefins, phenolic organic compounds, and metal salts thereof. Preferred dispersing agents include the oil-soluble sulfonic acids, carboxylic acids, and metal salts thereof.

Sulfonates which are suitable are oil-soluble and include alkyl sulfonates, alkaryl sulfonates, the so-called mahogany or natural soaps, and the like. The mahogany soaps include, particularly, the oil-soluble aromatic sulfonates from petroleum. Many of the aromatic sulfonates have cycloalkyl (i.e., naphthenic) groups in the side chains attached to the benzene ring. The mahogany soaps may include nonaromatic sulfonates produced in

conventional sulfuric acid refining of lubricating oil distillates and from the industrial use of fuming sulfuric acid in the refining of petroleum. The industrial production of oil-soluble mahogany sulfonates from petroleum is well understood in the art and is described in the literature. Normally, the alkyl sulfonates require about 24 carbon atoms for oil solubility. The alkaryl sulfonates, however, require an alkyl portion totaling only about 18 carbon atoms. To attain the requisite oil solubility, therefore, requires that the hydrocarbon portion of the sulfonate have a molecular weight between about 350 and 1,000. Preferably, this molecular weight is between 400 and 700. Particularly useful sulfonates include diwaxbenzene sulfonates, diwaxtoluene sulfonates, and postdodecylbenzene sulfonates. Postdodecylbenzene, which consists of monoalkylbenzenes and dialkylbenzenes in the approximate mole ratio of 2 to 3, has typical properties as follows:

Specific gravity at 38° C.		0.8649
Average molecular weight		385
Percent sulfonatable		88
A.S.T.M. D–158 Engler:		
I.B.P.	° F	647
5	do	682
50	do	715
90	do	760
95	do	775
F.B.P.	do	779
Refractive index at 23° C.		1.4900
Viscosity at:		
—10° C.	centipoises	2800
20° C.	do	280
40° C.	do	78
80° C.	do	18
Aniline point	° C	69
Pour point	° F	—25

The wax used in making the wax aromatic sulfonate is obtained from different sources of crude petroleum oil. Various grades of paraffin wax are made with different melting points. The 126–128° F. (52.2–53.3° C.) melting point wax is a mixture of organic compounds with the molecular weight averaging in the range of 330–340. The average number of carbon atoms in this mixture of organic compound will be around 24. As the melting point of the wax decreases, the carbon content of the mixture will average as low as 18 or a little lower.

Other sulfonates which may be used in the process of this invention include, for example, mono- and poly-wax substituted naphthalene sulfonates, dinonyl naphthalene sulfonates, diphenyl ether sulfonates, naphthalene disulfide sulfonates, diphenyl amine sulfonates, dicetyl thianthrene sulfonates, dilauryl beta-naphthol sulfonates, dicapryl nitro-naphthalene sulfonates, unsaturated paraffin wax sulfonates, hydroxy substituted paraffin wax sulfonates, tetra-amylene sulfonates, mono- and poly-chloro substituted paraffin wax sulfonates, nitrosoparaffin wax sulfonates; cycloaliphatic sulfonates, such as lauryl-cyclohexyl sulfonates, mono- and poly-wax substituted cyclohexyl sulfonates, and the like. The expression "petroleum sulfonate" is intended to cover all sulfonates derived from petroleum products.

Instead of using the foregoing sulfonates as such in the invention, we may also form those sulfonates in situ by adding the corresponding sulfonic acid to the mixture, which sulfonic acid then can be converted to the sulfonate by any convenient means.

Suitable carboxylic acids include naphthenic acids such as the substituted cyclopentane monocarboxylic acids, the substituted cyclohexane monocarboxylic acids and the substituted aliphatic polycyclic monocarboxylic acids containing at least 15 carbon atoms. Specific examples include cetyl cyclohexane carboxylic acids, dioctyl cyclopentane carboxylic acids, dilauryl decahydronaphthalene and stearyl-octahydroindene carboxylic acids, and the like, and oil-soluble salts thereof. Suitable oil-soluble fatty acids are those containing at least 8 carbon atoms. We prefer fatty acids which are liquids at ambient temperatures down to about 15° C. Specific examples include 2-ethyl hexanoic acid, pelargonic acid, oleic acid, palmitoleic acid, linoleic acid, and ricinoleic acid. Naturally occurring mixtures of predominately unsaturated fatty acids, such as tall oil fatty acids, are particularly suitable. Similarly, as in the case of the sulfonates, instead of using the foregoing carboxylic acid soap as such, we may form those soaps in situ by adding the corresponding carboxylic acid to the mixture.

The phosphorus sulfide treated olefins (by the term "olefins" we mean to include also olefin polymers, e.g., polyisobutylene) and their oil-soluble metal salts which are suitable for use include those customarily used in lubricating oil formulations as corrosion inhibitors and/or detergents. Specifically, they include the potassium-polyisobutylene-phosphorus sulfide products described by U.S. Patent 2,316,080, issued on April 6, 1943, to Loane and Gaynor, and a similar material containing no metal made by addition of a phosphorus sulfide to wax olefins, as described in U.S. Patent 2,516,119, issued on July 25, 1950, to Hersh. This latter preferred material is made by first forming wax olefins from paraffin waxes by halogenation and dehydrohalogenation and subsequently treating the olefins with a phosphorus sulfide, preferably phosphorus pentasulfide. Another teaching of the preparation of phosphorus sulfide treated olefins is Patent 2,688,612, issued September 7, 1954, to Watson.

The phenolic organic compounds which may be used are the free oil-soluble phenolic compounds or the metal phenates thereof. Oil-solubility is imparted to such phenolic compounds by the presence in the molecule of at least nine aliphatic carbon atoms. Specific examples are: 3,5,5-trimethyl-n-hexyl phenol, n-decyl phenols, cetyl phenols, nonyl phenols, and the like; alkaryl substituted phenols such as alkyl-phenyl phenols; polyhydroxy alkyl-aromatic compounds such as 20-carbon alkyl resorcinol, or poly-hydroxy alkyl-benzenes, such as, for example, octyl catechol, triiso-butyl pyrogallol, and the like; monohydroxy alkyl-naphthalenes such as 12-carbon alkyl alpha naphthol, and the like. Alkyl substituted phenol sulfides containing at least 5-alkyl carbon atoms such as iso amyl or nonyl phenol disulfide and the like may be used. Dinonyl phenol and nonyl phenol disulfide have been found to be preferred materials.

While it has been noted previously that the prior art teaches the use of double decomposition reactions to prepare metal phenates, it should be emphasized that the present process uses a double decomposition reaction to prepare metal alkoxides. These metal alkoxides can then be used to prepare metal phenates containing excess of dispersed cations.

Some of the process conditions which are employed in the preparation of the basic metal compound-containing dispersions will now be discussed. In forming the dispersions, a mixture of the metal alkoxide or metal alkoxide-carbonate complex with the nonvolatile carrier, the dispersing agent and the water is produced. The amount of these several components can vary widely. The amount of water which is incorporated in the dispersion mixture initially will be determined by (a) the amount which is stoichiometrically required to hydrolyze the metal alkoxide or alkoxide-carbonate complex to the corresponding metal hydroxide, and (b) the amount of water in excess of such stoichiometric amount which is required to prevent the formation of a gel in the dispersion. The need for the presence of a stoichiometric excess of water is true in both a batch and a continuous process. It is not necessary that all of the water be added to the reaction vessel prior to the addition of the metal alkoxides or alkoxide-carbonate complex to the mixture. However, there should

always be a stoichiometric excess of water in the reaction vessel in order to prevent severe gel formation.

The overbasing step (that is, the addition of the metal alkoxide intermediate to the dispersing agent solution) is conducted over a wide range of temperatures, generally at about 25° C. to about 100° C., and more preferably in the range of about 35° C. to about 65° C. Temperatures outside the broad range (25° C. to 100° C.) are generally not used, since they can lead to gel formation or to the formation of inorganic insoluble materials.

Following the hydrolysis, the volatile materials (alcohol, solvent, and unreacted water) are removed by distillation from the reaction mixture. During the later stages of the distillation, it is often desirable to employ gas blowing to facilitate solvent removal. When it is desired to convert the majority of the metal hydroxide to the corresponding carbonate as previously explained, carbon dioxide is used for blowing. When it is desired to leave the majority of the dispersoid as the metal hydroxide, an inert gas such as nitrogen or helium is used for stripping purposes. The removal of the volatile solvent leaves a bright fluid product which requires no additional filtration or centrifugation.

The relative amounts of the different components employed in the process are dependent upon the desired percent actives and upon the base numbers desired in the final compositions. (The term "percent active" refers to the amount of the dispersing agent present in the composition.)

In order to disclose more clearly the nature of the present invention, the following illustrative examples are given, in which all percentages are by weight. Also, all the base numbers of the products to which reference is made were determined by the acetic acid titration method which utilizes glacial acetic acid as the solvent, and a solution of perchloric acid in glacial acetic acid as the titrant. The method is especially adapted for a determination of this type since equilibria are obtained rapidly. The procedures for carrying out acetic acid titrations are generally outlined in Analytical Chemistry, Volume 23, No. 2, February 1951, page 337, and Volume 24, No. 3, March 1952, page 519. As used herein, base number refers to milligrams of potassium hydroxide per gram of sample.

In some of the examples which follow, particularly where an amphoteric metal is employed, determination of the base number is not possible. To provide a basis of comparison, the theoretical base number is calculated from the metal content.

EXAMPLE 1

Preparation of calcium alkoxide and calcium alkoxide-carbonate complex

A one-liter, three-necked flask equipped with a mechanical stirrer, condenser, thermometer, and dropping funnel was charged with 23 grams of metallic sodium and 450 grams of isobutyl alcohol. This mixture was stirred at 85–90° C. until all of the metallic sodium had reacted. The reaction mixture was cooled and was then added dropwise to 55.5 grams of anhydrous calcium chloride dissolved in 285 grams of isobutyl alcohol. A white precipitate formed immediately upon the addition. This mixture was then refluxed for two hours. Following the refluxing of the mixture, carbon dioxide was bubbled through the mixture to completely solubilize the calcium alkoxide and to form the calcium isobutyl carbonate. The mixture was then filtered through Hyflo (a filter aid material made of exceptionally pure diatomaceous earth and sold by the Johns-Manville Sales Corporation, New York, New York) to yield 565 grams of a clear pale yellow liquid. Upon analysis, the filtrate was found to contain 3.60 percent calcium present as calcium isobutyl carbonate, which corresponds to over 95 percent utilization of the calcium chloride initially present.

EXAMPLE 2

Preparation of sodium methoxy ethoxide without using an added azeotroping agent

A suitable vessel was equipped for fractional distillation. To this vessel was charged 1,100 parts of "methyl Cellosolve" and 208.8 parts of anhydrous sodium hydroxide. This mixture was heated until reflux conditions were obtained. At this point the overhead temperature was 68° C. and the bottoms temperature was 140° C. The overhead condensate was removed at a reflux ratio of 10 to 1 over an extended period. During this time the temperatures of both the overhead and bottoms gradually rose. After the water of reaction had been removed the overhead temperature was 122° C. and the bottoms temperature was 166° C. A total of 252.7 parts of overhead liquid was collected. This mixture was found to contain 36.8 percent water. This corresponds to over 99 percent of the theoretical water of reaction.

EXAMPLE 3

Preparation of calcium methoxy ethoxide and calcium methoxy ethoxide-carbonate

To a one-liter flask equipped for azeotropic distillation was added 380 grams of "methyl Cellosolve" (a monomethyl ether of ethylene glycol), 40 grams of sodium hydroxide, and 100 grams of benzene. This mixture was refluxed to azeotropically remove the water formed by the reaction along with a portion of the "methyl Cellosolve." A benzene insoluble liquid, in the amount of 31.9 grams, was recovered from the azeotropic trap. This mixture contained approximately 45 percent "methyl Cellosolve" and 55 percent water. This amount of water corresponds to over 98 percent of the amount which should theoretically be yielded by the sodium hydroxide "methyl Cellosolve" reaction. To the alcoholic sodium alcoholate solution was then added 55 grams of calcium chloride. This mixture was then refluxed for two hours, allowed to cool, and 22 grams of carbon dioxide was added to it by bubbling the gas through the reaction mixture over a twenty-minute period. The carbon dioxide was added as a gas below the surface of the liquid with stirring. The benzene was then removed from the mixture by distillation, and the calcium alkoxide solution was filtered. Three hundred and fifty-three grams of the filtrate was recovered and was a clear, light yellow liquid containing 5.66 percent calcium. This intermediate contained only 0.1 percent chloride and represents a conversion of over 95 percent of the calcium chloride to calcium methoxy ethoxide-carbonate.

EXAMPLE 4

Preparation of magnesium methoxy ethoxide-carbonate

The preparation of this product was carried out in the same manner as in Example 3, except that an equivalent amount of magnesium chloride was used instead of the calcium chloride. This yielded 381 grams of a clear, light yellow liquid which contained 3.01 percent magnesium and less than 0.1 percent chloride.

EXAMPLE 5

Preparation of zinc methoxy ethoxide

The preparation of this product was carried out in the same manner as in Example 3, except that an equivalent amount of zinc chloride was used instead of calcium chloride and that the alkoxide was not converted to the carbonate. Also, the benzene was not stripped from the reaction mixture. This yielded 455 grams of a clear, pale yellow liquid containing 7.03 percent zinc.

EXAMPLE 6

Preparation of copper methoxy ethoxide

The preparation of this product was carried out in the same manner as in Example 3 except that the alkoxide was not converted to the carbonate and that an equivalent

amount of cupric chloride was used instead of calcium chloride. A dark green liquid was obtained which contained 2.34 percent copper as the copper methoxy ethoxide.

EXAMPLE 7

Preparation of barium methoxy ethoxide

The preparation of the barium methoxy ethoxide product was carried out in the same manner as in Example 3 except that the alkoxide was not converted to the carbonate and that an equivalent amount of barium chloride was used instead of calcium chloride. Three hundred and forty grams of a dark colored liquid containing 11.7 percent barium as the methoxy ethoxide was yielded.

EXAMPLE 8

Preparation of aluminum methoxy ethoxide

A 500-milliliter flask equipped with a condenser, thermometer, mechanical stirrer, and dropping funnel was charged with 12.5 grams of anhydrous aluminum sulfate and 100 grams of "methyl Cellosolve." This mixture was heated to 50° C. and 100 grams of a sodium methoxy ethoxide solution was added dropwise with stirring. The mixture was refluxed for two hours, and then 125 grams of the "methyl Cellosolve" was removed by distillation. After filtration, this yielded a clear, pale yellow liquid, weighing 70.5 grams and contained 2.84 percent aluminum.

EXAMPLE 9

Preparation of nickel methoxy ethoxide

To a one-liter flask equipped for azeotropic distillation were charged 30.9 grams of sodium hydroxide, 400 milliliters of "methyl Cellosolve" and 150 milliliters of benzene. A total of 27.3 milliliters of benzene insoluble liquid was removed from the reaction mixture by azeotropic distillation. The reaction mixture was cooled slightly, and then 59.7 grams of nickel sulfate were added, and the mixture was refluxed for four hours. The insoluble solids were removed by filtration to yield a greenish-brown solution containing 3.04 percent nickel.

EXAMPLE 10

Preparation of nickel methoxy ethoxide

To a 12-liter flask equipped with a fritted tube and an azeotropic distillation trap were charged 4800 milliliters of "methyl Cellosolve" and 1800 milliliters of benzene. Nitrogen was blown through the fritted tube to purge the system of oxygen. Five hundred grams of sodium hydroxide were then added to the benzene-alcohol mixture and the system was heated to reflux. A benzene insoluble liquid in the amount of 450 milliliters was removed by azeotropic distillation. The reaction mixture was then cooled while purging with nitrogen to maintain the light color of the sodium alkoxide solution.

To a second 12-liter flask equipped with mechanical stirrer, dropping funnel, and reflux condenser were charged 1000 milliliters of "methyl Cellosolve" and 810 grams of nickel chloride. The sodium alkoxide alcoholic solution in the first flask was then added to the contents of the second flask over a period of four hours and fifteen minutes. During the addition, the reaction mixture was stirred and the temperature was maintained at 90–105° C. in the reaction flask. The preparation was held at the reflux temperature for four hours, cooled, allowed to settle, and then filtered through "Hyflo" to remove the solids. The filtered product weighed 6415 grams and contained 5.76 percent nickel. This represents 100 percent utilization of the available nickel.

EXAMPLE 11

Preparation of cobalt methoxy ethoxide-carbonate

To a one-liter flask equipped for azeotropic distillation were added 30.9 grams of sodium hydroxide, 400 milliliters of "methyl Cellosolve," and 150 milliliters of benzene. A total of 27.3 milliliters of benzene insoluble liquid was removed from the mixture of azeotropic distillation. The reaction mixture was then cooled and 59 grams of cobalt chloride were added. The reaction mixture was held at reflux temperature overnight and was then filtered to remove insoluble solids. A deep blue solution, weighing 451.4 grams and containing 5.08 percent cobalt, was recovered. After standing for a short period of time, some of the cobalt methoxy ethoxide began to precipitate from the solution. The solution was therefore stabilized by blowing with carbon dioxide to form the deep violet colored cobalt methoxy ethoxide-carbonate.

EXAMPLE 12

Preparation of cobalt methoxy ethoxide-carbonate

To a one-liter flask equipped with a mechanical stirrer and equipped for azeotropic distillation were added 30.9 grams of sodium hydroxide, 108.2 grams of hydrated cobalt chloride ($CoCl_2 \cdot 6H_2O$), 400 milliliters of "methyl Cellosolve," and 1500 milliliters of benzene. The reactants were stirred and heated, and 82 milliliters of benzene insoluble liquid were removed by azeotropic distillation. The product was filtered through "Hyflo" to yield 341.5 grams of a bright blue solution. Solids began to form immediately, but the solution was stabilized by blowing with carbon dioxide to form the deep violet-colored cobalt methoxy ethoxide-carbonate which contained 1.32 percent cobalt.

EXAMPLE 13

Preparation of manganese methoxy ethoxide

To a 500-milliliter flask equipped with mechanical stirrer, dropping funnel, thermometer, and reflux condenser were charged 30.6 grams of manganous sulfate and 50 milliliters of "methyl Cellosolve." The contents of the flask were then heated to between 90–100° C., and 207.6 grams of sodium methoxy ethoxide containing 4.5 percent sodium were added over a period of about two hours. The mixture was held at reflux for two hours, cooled, and filtered through "Hyflo" to yield 204.9 grams of a dark solution containing 0.65 percent manganese.

EXAMPLE 14

Preparation of cadimum methoxy ethoxide

Preparation of this product was carried out in the same manner as in Example 13, except that 36.7 grams of cadmium sulfate was charged to the reaction flask instead of the manganous sulfate, and 180 grams of sodium methoxy ethoxide containing 4.5 percent sodium were then added to the flask. The filtered product which was obtained weighed 171.5 grams and contained 1.62 percent cadmium.

EXAMPLE 15

Preparation of chromium methoxy ethoxide

The preparation of this product was carried out in the same manner as in Example 14, except that 19.6 grams of chromic chloride were charged to the reaction flask and 190.6 grams of sodium methoxy ethoxide containing 4.5 percent of sodium were added and the mixture stirred. Approximately 180 grams of the filtered product were obtained and contained 1.41 percent chromium.

EXAMPLE 16

Preparation of oil-soluble dispersion containing basic nickel compounds

To a one-liter, three-necked flask equipped with mechanical stirrer, dropping funnel, thermometer, and reflux condenser were charged 100 grams of postdodecylbenzene sulfonic acid, 33.8 grams of 100 pale oil, 4.55 grams of water, and 45 grams of benzene. By analysis, the postdodecylbenzene sulfonic acid had a total acidity of 0.623

milliequivalents/gram, a sulfonic acidity of 0.592 milliequivalents/gram, and contained 48.8 percent nonvolatiles and 26.6 percent sulfonic acid. By difference, the free oil in the acid amounted to 22.2 percent. The amount of water used represented 1.5 times the theoretical amount required to hydrolyze all of the nickel methoxy ethoxide which was available for overbasing. The benzene was added as a processing solvent, and is not necessary to the reaction. The above mixture was heated, with stirring, to 50° C. and 243.8 grams of nickel methoxy ethoxide containing 2.74 percent nickel were added to the reaction mixture through a dropping funnel having a tip protruding below the surface of the reaction mixture. The flask contents were held at the reflux temperature for thirty minutes before solvent removal. The solvents were removed while heating the flask contents up to 150° C., whereupon carbon dioxide blowing was commenced while maintaining the temperature at approximately 150° C. The bright, green-brown fluid obtained weighed 93.7 grams, was 30 percent active as nickel sulfonate and, by analysis, contained 7.34 percent nickel and had an acetic base number of 102.

EXAMPLE 17

Preparation of an oil soluble dispersion containing a basic nickel compound as the dispersoid

To a one-liter flask equipped as described in Example 16 were charged 25 grams of a tall oil fatty acid (3.39 milliequivalents of acid per gram), 54.5 grams of 100 pale oil, 45 grams of benzene, and 3.24 grams of water. This amount of water was 1.1 times the theoretical amount required to completely hydrolyze the nickel which was available for over-basing. The benzene was present as a process solvent. The reaction mixture was heated to 50° C., and 266 grams of nickel methoxy ethoxide containing 2.74 percent nickel were added. The flask was equipped for distillation, and the solvents were removed to a flask content temperature of 150° C. Carbon dioxide blowing was then used to carbonate the overbasing material and assist in solvent removal. The bright green product weighed 93.3 grams and contained 7.74 percent nickel. This corresponds theoretically to the anticipated 30 percent active, 100 base number product.

EXAMPLE 18

Preparation of an oil-soluble dispersion containing basic zinc compounds

To a one-liter flask, equipped as described in Example 16, were charged 200 grams of postdodecylbenzene sulfonic acid (same as in Example 16), 66.0 grams of 100 pale oil, and 6.6 grams (150 percent of the stoichiometric amount required) of water. A total of 167 grams of zinc methoxy ethoxide containing 7.02 percent zinc were added over a twenty-five minute period at a temperature of 47° C. The mixture was heated to 150° C. and the volatile solvents removed. The product was then blown with carbon dioxide for about twenty minutes at 150° C. The product was a bright fluid and had a light yellow color. This procedure produced a 30 percent zinc sulfonate dispersion with a base number of 50, which contained 6.1 percent zinc. The particle size as determined by electron microscope of the zinc sulfonate was less than 0.1 micron.

EXAMPLE 19

Preparation of an oil-soluble dispersion containing basic nickel compound as the dispersoid

To a one-liter flask equipped as described in Example 16 were charged 25 grams of 2-ethyl hexanoic acid, 12.5 grams of pale oil, 100 milliliters of benzene, and 1.95 grams of water. This amount of water was 1.1 times the theoretical amount required to completely hydrolyze the nickel which was available for overbasing. The benzene served as a process solvent. The reaction mixture was heated to 51° C., and 153.7 grams of nickel methoxy ethoxide containing 5.19 percent nickel were added. The flask was equipped for distillation, and the solvents were removed to a flask content temperature of 165° C. Nitrogen blowing was used to assist in solvent removal. The flask contents were then lowered to 153° C. and carbon dioxide blowing was utilized to carbonate the overbasing material. After cooling, 35 milliliters of isopropanol were added to improve the fluidity. The 81.2 grams of product were filtered through "Hyflo," and the bright green product containing 10.14 percent nickel. This corresponds to a theoretical 63 base number product.

The particles in the dispersons produced by the present invention have been described as being colloidal in size. This term is meant to include particles in the range of 0.001 to 1.0 micron.

While particular embodiments of the invention have been described, it will be understood, of course, that the invention is not limited thereto, since many modifications may be made in the process conditions and reactants used; and it is therefore contemplated to cover by the appended claims any such modifications as fall within the true spirit and scope of the invention.

The invention having thus been described, what is claimed and desired to be secured by Letters Patent is:

1. A process of preparing a stable dispersion of metal compounds, wherein the metal thereof is selected from the group consisting of cobalt, silver, arsenic, bismuth, cadmium, chromium, copper, iron, mercury, manganese, molybdenum, nickel, lead, antimony, tin, vanadium, zinc and zirconium, in a non-volatile carrier, which process comprises:

(a) admixing an alcohol-soluble metal-containing intermediate selected from the group consisting of cobalt alkoxide-carbonate complexes and metal alkoxides, wherein the metal of said metal alkoxide is selected from the group consisting of silver, arsenic, bismuth, cadmium, chromium, copper, iron, mercury, manganese, molybdenum, nickel, lead, antimony, tin, vanadium, zinc and zirconium, an oil-soluble dispersing agent, a nonvolatile carrier, and water, in an amount in excess of the stoichiometric amount required to hydrolyze all of said alcohol-soluble metal containing intermediate;

(b) hydrolyzing the alcohol-soluble metal-containing intermediate to an oil-insoluble metal compound; and

(c) removing the volatile materials from said admixture,

said process being characterized further in that the cobalt alkoxide-carbonate complex and the metal alkoxide of step (a) are prepared by a process comprising:

(i) reacting an alcohol solution of an alkali metal alkoxide, wherein the alkoxide radical is selected from the group consisting of alkoxide radicals derived from monoethers of ethylene glycol containing not more than 8 carbon atoms and alkoxide radicals derived from monoethers of diethylene glycol containing not more than 8 carbon atoms, with a metal salt, wherein the metal of said metal salt is selected from the group consisting of cobalt and the metals defined in step (a) above, to form an alkoxide of the metal of said metal salt, said metal salt being characterized further in that the corresponding alkali metal salt is less soluble in the alcohol solution than is said metal salt.

said process being characterized still further in that the preparation of the colbalt alkoxide-carbonate complex includes the additional step of blowing the solution containing cobalt alkoxide with carbon dioxide to form said cobalt alkoxide-carbonate complex.

2. The process described in claim **1** characterized further in that in step (i) the anion of said metal salt is selected from the group consisting of halide, nitrate, sulfate, acetate, ammonium phosphate, bromate, carbonate, citrate, cyanide, dithionate, formate, iodate, nitrite, oxy-

late, phosphate, silicate, sulfide, sulfite, tartrate, aluminate, antimonate, arsenate, bismuthate, borate, chromate, manganate, molybdate, selenate, tungstate, uranate, and vanadate.

3. The process described in claim 2 characterized further in that in step (a) the oil-soluble dispersing agent is selected from the group consisting of sulfonic acids, metal sulfonates, carboxylic acids, metal carboxylates, phosphorus sulfide-treated olefins, metal salts of phosphorus sulfide-treated olefins, phenolic organic compounds, and metal salts of phenolic organic compounds.

4. The process described in claim 3 characterized further in that in step (a) the nonvolatile carrier is selected from the group consisting of mineral lubricating oils and synthetic lubricating oils.

5. The process described in claim 4 characterized further in that the metal of said metal compound, and of said metal alkoxide, is selected from the group consisting of cadmium, copper, chromium, manganese, nickel and zinc.

6. The process described in claim 5 characterized further in that the metal alkoxide is derived from methoxy ethanol.

7. The process described in claim 6 characterized further in that the oil-soluble dispersing agent is selected from the group consisting of oil-soluble sulfonic acids and oil-soluble metal sulfonates.

8. The process described in claim 7 wherein the metal is cadmium.

9. The process described in claim 7 wherein the metal is copper.

10. The process described in claim 7 wherein the metal is chromium.

11. The process described in claim 7 wherein the metal is manganese.

12. The process described in claim 7 wherein the metal is nickel.

13. The process described in claim 7 wherein the metal is zinc.

14. The process of preparing a stable dispersion of metal compounds, wherein the metal thereof is selected from the group consisting of cobalt, silver, arsenic, bismuth, cadmium, chromium, copper, iron, mercury, manganese, molybdenum, nickel, lead, antimony, tin, vanadium, zinc and zirconium, in a nonvolatile carrier, which process comprises:

(a) admixing an alcohol-soluble metal-containing intermediate selected from the group consisting of cobalt alkoxide-carbonate complexes and metal alkoxides, wherein the metal of said metal alkoxide is selected from the group consisting of silver, arsenic, bismuth, cadmium, chromium, copper, iron, mercury, manganese, molybdenum, nickel, lead, antimony, tin, vanadium, zinc and zirconium, an oil-soluble dispersing agent selected from the group consisting of sulfonic acids and metal sulfonates, a nonvolatile carrier selected from the group consisting of mineral lubricating oils and synthetic lubricating oils, and water, in an amount in excess of the stoichiometric amount required to hydrolyze all of said alcohol-soluble metal-containing intermediate in the admixture;

(b) hydrolyzing the alcohol-soluble metal-containing intermediate; and

(c) removing the volatile materials from said admixture;

said process being characterized further in that the cobalt alkoxide-carbonate complex and the metal alkoxide of step (a) are prepared by a process comprising:

(i) reacting an alkali metal hydroxide with an alcohol selected from the group consisting of monoethers of ethylene glycol containing not more than 8 carbon atoms and monoethers of diethylene glycol containing not more than 8 carbon atoms to form an alkali metal alkoxide and water in said alcohol,

(ii) removing water from the reaction mixture by azeotropic distillation, and

(iii) reacting a metal salt, wherein the metal of said metal salt is selected from the group consisting of cobalt and the metals defined in step (a) above and wherein the anion of said metal salt is selected from the group consisting of halide, nitrate, sulfate, acetate, ammonium phosphate, bromate, carbonate, citrate, cyanide, dithionate, formate, iodate, nitrite, oxylate, phosphate, silicate, sulfide, sulfite, tartrate, aluminate, antimonate, arsenate, bismuthate, borate, chromate, manganate, molybdate, selenate, tungstate, uranate and vanadate, with the alkali metal alkoxide of step (ii) to form an alkoxide of the metal of said metal salt, said metal salt being characterized further in that the corresponding alkali metal salt is less soluble in the alcohol solution than in said metal salt,

said process being characterized still further in that the preparation of the cobalt alkoxide-carbonate complex includes the additional step of blowing the solution containing cobalt alkoxide with carbon dioxide to form said cobalt alkoxide-carbonate complex.

15. The process described in claim 14 characterized further in that the alkoxide radical is derived from methoxy ethanol.

16. The process described in claim 15 characterized further in that the metal is selected from the group consisting of cadmium, copper, chromium, manganese, nickel, and zinc.

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