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SALTS OF CERTAIN METHYLENE DIAMINES WITH CERTAIN PETROLEUM SULPHONIC ACIDS

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2 Claims. (Cl. 260—501)

This invention relates to a new composition of matter consisting of a certain kind of amine salt derived from water-soluble petroleum sulphonic acid or acids of the kind hereinafter described.

The main object of my invention is to provide a new material or composition of matter that is an efficient solubilizer, particularly in instances where it is desired to make two immiscible materials mutually soluble, and which is also capable of use as a demulsifier for crude oil emulsions, either alone, or in admixture with conventional demulsifying agents, such for example, as demulsifying agents of the modified fatty acid type, or of the alkylated aromatic sulphonic acid type.

Petroleum sulphonic acids are produced from a wide variety of petroleum distillates or petroleum fractions, and in some instances, they are produced from the crude petroleum itself. When produced from crude petroleum itself, it is customary to use crude oil of the naphthene type, crude oil of the paraffin type, crude oil of the asphaltic type and mixtures of said three different types of crude oil.

The art of refining petroleum crude or various fractions, using sulphuric acid of various strengths, as well as monohydrate and fuming acid, is a well known procedure. In such conventional refining procedure, petroleum sulphonic acids have been produced as by-products. For instance, in removing the olefinic components, it has been common practice to use sulphuric acid, so as to polymerize the olefines or convert them into sulphonic acids which are subsequently removed. Likewise, in the production of white oil or highly refined lubricating oils, it has been customary to treat with fuming sulphuric acid, so as to eliminate certain undesirable components.

In recent years, certain mineral oil fractions have been treated with sulphuric acid with the primary object of producing petroleum sulphonic acids, and in such procedure the petroleum sulphonic acids represented the primary objects of reaction, rather than concomitant by-products.

Petroleum sulphonic acid, regardless of whether derived as the principal product of reaction or as a by-product, can be divided into two general types, to wit, green acid or acids and mahogany acid or acids. The green acids are characterized by being water-soluble or dispersible. In other words, they form either true solutions or sols. For purpose of convenience, they will be herein referred to as water-soluble without any effort to indicate whether the solution is molecular or colloidal in nature. The green acids, as indicated by their name, frequently give an aqueous solution having a dark green or grey-green appearance. They generally appear as a component of the acid draw-off and do not remain behind dissolved in the oil fraction which has been subjected to sulphuric acid treatment. The green acids are not soluble in oil, even when substantially anhydrous, and certainly are not soluble in oil when they contain as much as 15% of water. Similarly, their salts obtained by neutralization with a strong solution of caustic soda, caustic potash, or ammonia, are not oil-soluble. For convenience of classification, the ammonium salt will be considered as an alkali salt.

In contradistinction to the hydrophile green acids, there occurs, as in the manufacture of medicinal white oil, the oil-soluble type or the mahogany acids. These mahogany acids are characterized by being soluble in oil, especially when anhydrous, and being soluble in oil, even if they contain some dissolved water. Some of the mahogany acids also show limited hydrophilic properties to the extent that either some water can be dissolved in the acids, or they, in turn, may dissolve to some extent in water. In some instances their salts, such as the sodium, ammonium, or potassium salt, will dissolve in water to give a colloidal sol. However, regardless of the presence of any hydrophilic properties whatsoever, they always have a characteristic hydrophobe property, as indicated by the fact that the substantially anhydrous form, for instance, their alkali salts containing 5–12% water, will dissolve in oil. This clearly distinguishes them from the green acids previously referred to, because the green acids in similar form containing the same amount of water, for example, will not dissolve in oil. The green acids, as such, are essentially hydrophilic and non-hydrophobic in character.

The utility of the mahogany acids in various arts has been enhanced by increasing their water solubility; for instance, converting the mahogany acids into hydroxy alkylamine salts. On the other hand, as far as I am aware, no valuable product of commerce has resulted from decreasing the water solubility of the mahogany acids by the addition of some oil-soluble basic amine, such, for example, as triamylamine. The triamylamine salts of mahogany acids, for example, are completely devoid of any solubility in water which the alkali salts may have exhibited and show, as would be expected, an increased solubility in hydrophobe solvents.

Green acids are hydrophile in character, as

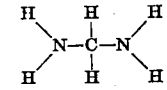
previously stated. Their hydrophile character has been increased by neutralization with materials such as triethanolamine and the like. Such green acid salts having enhanced water solubility, as compared with the ordinary alkali salts, have found application in certain arts.

I have found that when green acids, i. e., the oil-insoluble type, are neutralized with a diamine of the kind hereinafter described, so as to produce a water-insoluble product, that the resulting material, even though it does not exhibit any marked oil solubility, especially when it contains 5–10% of water, still has pronounced value as a demulsifier for oil field emulsions, either when used alone, or in conjunction with other known demulsifying agents. I employ diamines of the kind derivable most readily by reactions involving an aldehyde and a secondary amine, all of which is hereinafter described in detail. I have also found that sometimes such amine salt of green acids will mix in with a hydrophobe material and a hydrophile material, so as to produce a homogeneous mixture. The effectiveness of the above described material or composition of matter as a demulsifying agent for oil field emulsions appears to be related to some factor other than its solubility characteristics.

The new composition of matter which constitutes my present invention is represented by amine salts of hydrophilic, non-hydrophobic green petroleum acids, as exemplified by the salt derived from such green acids by neutralization with the diamine obtained by reaction between two moles of diamylamine and one mole of formaldehyde or one mole of acetaldehyde. The manufacture of said composition of matter involves nothing more or less than neutralizing one mole of the selected petroleum acid with a mole of a suitable amine, or neutralizing two moles of the selected petroleum sulphonic acid with one mole of the amine, in that the amine being a diamine, is dibasic. In the latter case, a suitable indicator, such as methyl orange indicator, may be employed. For purposes of convenience, I prefer that the selected petroleum sulfonic acid contain not over 15% of water. It is understood, of course, that the conventional procedure, employing double decomposition instead of direct neutralization, can be utilized in the manufacture of my new material or composition of matter. For instance, the sodium salt of the selected petroleum sulfonic acid can be dissolved in alcohol or other suitable solvent, and the amine hydrochloride added so that sodium chloride will precipitate. After filtering off the precipitated sodium chloride, the alcohol can be evaporated and the amine salt recovered. If desired, a mixture of amines instead of a single amine may be employed.

It is well known that certain monocarboxy organic acids, containing approximately eight carbon atoms or more, and not more than thirty-two carbon atoms, are characterized by the fact that they combine with alkalies to produce soap or soap-like materials. These detergent-forming acids include fatty acids, resin acids, petroleum acids, etc. For the sake of convenience, these acids will be indicated by the formula R.COOH.

It is also well known that diamines, having pronounced basic properties, may be derived by various means, provided that the resultant diamine is characterized by the fact that the two amino nitrogen atoms are not attached to the same carbon atom. Such diamines, generally referred to as alkylene diamines, are well known and may be characterized by ethylene diamine. Derivatives of the diamines herein contemplated are characterized by being a methylene diamine derivative, i. e., a derivative of the hypothetical methylene diamine



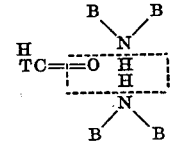
Methylene diamine is almost unknown for practical purposes, since it is very unstable in the form of a free base, but does exist in the form of alkylated or acylated derivatives. In view of this fact it becomes obvious that the new chemical compound or composition of matter previously referred to must necessarily be obtained indirectly, insofar that the parent diamine is almost non-existent.

It is well known that a large number of secondary amines are available, which may be designated by the formula type:

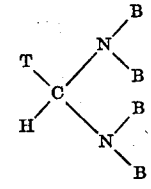


in which B represents an alkyl, aralkyl, alicyclic, alkylol, aralkylol, hydroxy alicyclic, heterocyclic, or other equivalent radical. B and B jointly may represent one radical, as in piperidine.

It is well known that aldehydes, particularly the aldehydes of relatively low molecular weight, such as formaldehyde, acetaldehyde, aldol, furfural, benzaldehyde, hexahydrobenzaldehyde, phenyl-acetaldehyde, etc., can combine with two moles of a secondary amine, so as to yield a methylene diamine, characterized by the fact that the two amino nitrogen atoms are attached to the same carbon radical. Such reaction may be indicated in the following manner:



The amine so produced may be indicated by the following formula:

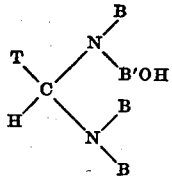


in which, as has been previously pointed out, T may represent a hydrogen atom derived from formaldehyde, or may represent a radical derived from acetaldehyde, propionaldehyde, butryaldehyde, heptaldehyde, lauric aldehyde, palmitic aldehyde, or stearic aldehyde.

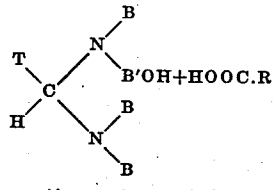
Similarly, instead of aliphatic aldehydes, one may employ heterocyclic aldehydes, such as furfuraldehyde, or aromatic aldehydes, such as benzaldehyde. Unsaturated aldehydes, such as acrolein, crotonaldehyde, or tiglic aldehydes, may be employed. As previously indicated, B represents a radical, such as the methyl, ethyl, propyl, butyl, amyl, hexyl, octyl, decyl, hexadecyl, octadecyl, or a similar radical. Similarly, B may represent an aralkyl radical, such as a benzyl radical, ethyl benzyl radical, dimethyl benzyl radical, an alicyclic radical, such as the cyclohexyl, methyl cyclohexyl, etc.; likewise, B may repre-

sent a hydroxy ethyl, hydroxy propyl, hydroxy butyl, and similar radicals, such as a $C_6H_4C_2H_4OH$ radical, or a $C_6H_{10}OH$ radical. Other radicals include the furfural radical, or hydroxy derivatives thereof. Piperidine may be considered as a special adaptation in which one radical replaces two amino hydrogen atoms.

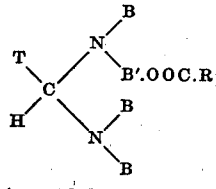
It is to be noted that the methylene diamine, expressed by the above formula, is a tertiary diamine in the sense that neither amino nitrogen atom has attached thereto a replaceable hydrogen atom. For convenience, the above formula may be rewritten as follows, so as to indicate such instances where there is present an alcoholic hydroxyl radical:



in which B'OH is obviously the monovalent hydroxy hydrocarbon radical, such as an alkylol radical or the like. Needless to say, B'OH may occur more than once, and B may occur less than three times. It is well known that amines such as triethanolamine or the like can be acylated by reaction with fatty acids or a suitable functional derivative thereof, such as the acyl chloride or the anhydride, or even the ester. If the tertiary hydroxy methylene diamine of the kind just described is reacted with a detergent-forming monobasic carboxy acid, the reaction may be indicated in the following manner:

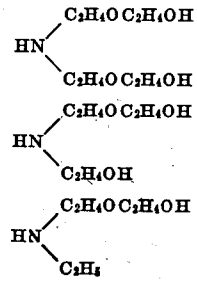


with the formation of an intermediate ester which may be indicated in the following manner:



In addition to aldol, other similar hydroxy aldehydes or aldehyde-alcohols may be employed. As to such aldehydes other than aldol, reference is made to Richter's Organic Chemistry, volume 1, Third English Edition, 1934, pages 389–391.

In view of what has been said previously, it does not appear necessary to enumerate various suitable amines which may be employed, but it may be well to indicate that among those which may be employed are the following: diethanolamine, dipropanolamine, dibutanolamine, dipentanolamine, dioctanolamine, glyceryl dihexanolamine, methyl glycerylamine, ethyl glycerylamine, propyl glycerylamine, cyclohexyl glycerylamine, benzyl glycerylamine; dibenzylamine, ethyl benzylamine, methyl benzylamine, propyl benzylamine, cyclohexyl ethylamine, cyclohexyl propylamine, cyclohexyl hexylamine, diethylamine, dipropylamine, diamylamine, dihexylamine, dioctylamine, diglycerylamine, etc. In all the previous examples, each radical indicates a substituent for an amino hydrogen atom. Similarly, amines can be obtained from polyglycerols or polyglycols, as for instance, the secondary amines, indicated by the following formulas:



Such amines may serve as functional equivalents of the previously described amines, which happen to be free from an ether linkage. Likewise, one may have amines in which there is more than one ether linkage, i. e., in which the hydrocarbon radical, which replaces an amino hydrogen atom, has been interrupted more than once by an oxygen atom.

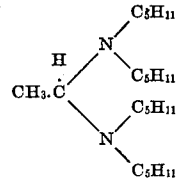
In examining the previous formulaes, it becomes evident that if two different amines are employed, the reaction is not limited to the two dissimilar amines, but may take place in part in such a manner as to involve two similar amines. In other words, if the two different amines be indicated as A and B, the reaction is not limited to the diamine involving both A and B, but in part the diamine will be formed solely from two molecules of A, and in part solely from two molecules of B. For practical purposes, then, it is most expedient, in the majority of instances, to manufacture or produce a methylene diamine from a single kind of secondary amine; and in such event, everything else being equal, it is most desirable to use the cheapest secondary amine available that will produce at least a fairly water-insoluble product, and the cheapest aldehyde available. I particularly prefer to use diethanolamine and to completely or at least partially esterify the diethanolamine with a long chain carbon atom acid, particularly a detergent-forming acid, having at least 8 carbon atoms and not more than 32 carbon atoms, such as oleic acid, naphthenic acid, or abietic acid. Naturally, the introduction of one or more of such long chain carbon compounds greatly increases the oil solubility of the amine; and such oil solubility is transposed, at least in part, to the final product, which is a salt of the sulphonic acid. As previously pointed out, it is not believed that oil solubility per se is the index as to effectiveness of the demulsifying agent. One may, of course, employ the hydroxylated diamine without acylation, but in such event, my experience has been that it is more preferable perhaps to employ diamylamine. Similarly, attention is again directed to the fact that wherever hydroxyl radicals exist, then such hydroxyl radical might be reacted with an acid having less than 8 carbon atoms, for instance, acetic acid, butyric acid, heptoic acid, etc. More than one hydroxy hydrocarbon radical, if present, may be acylated, and if two or more such redicals are reacted with acids, one need not employ the same acids, but different acids may be employed. A hydroxy radical attached to the aldehyde residue may be similarly acylated, as, for example, the residue

from aldol. A compound, such as sodium hydrogen phthalate, might be used for acylation.

My preferred reagent is manufactured in the following manner:

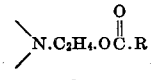
Two moles of diamylamine are cautiously reacted with a solution of formaldehyde, or preferably, with acetaldehyde, with cooling during the early stages to prevent the reaction from taking place too rapidly, and with a slight application of heat during the latter stages, so as to obtain complete reaction.

The methylene diamine so obtained may be indicated by the following formula:



If desired, of course, the product obtained by reaction can be purified in the customary manner, so as to remove any unreacted aldehyde, and also any unreacted simple secondary amine. However, if the reaction is conducted carefully, a substantial and generous yield of the desired diamine is obtained, and it is unnecessary to resort to any purification. It has been previously pointed out that having obtained an amine of the kind desired, it is only necessary to proceed to neutralize the green acid, as previously indicated.

Incidentally, it may be well to point out that one particularly desirable mixture of diamines is obtained by employing one mole of diethanolamine and one mole of diamylamine in connection with one mole of acetaldehyde. The resultant product so obtained will average two hydroxyl radicals per molecule; and one hydroxyl radical can be readily eliminated by acylation with one mole of a selected acid, particularly oleic acid or naphthenic acid. If desired, both hydroxyl radicals may be eliminated. In this instance the long carbon chain attached to an amino nitrogen atom is interrupted by an oxygen atom. It is understood in the hereto appended claims that reference to a hydrocarbon radical includes such radicals that are essentially hydrocarbon in nature, which include carbon atom chains that are interrupted at least once by an oxygen atom. This would occur, of course, in linkages such as the following:



where R is the hydrocarbon radical derived from naphthenic acid, oleic acid, acetic acid, heptoic acid, or the like. Acylation can be accomplished by any suitable acid compound, such as the acyl chloride, the anhydride, etc. If an amine salt is formed, such as the hydrochloride, it must be converted into a base by conventional treatment with strong caustic soda or the like.

Returning momentarily to the preparation of the preferred reagent, no additional information is required. However, it may be well to point out that I prefer to use a green acid selected so that it is relatively free from inorganic acid, such as sulphurous acid and sulphuric acid, and containing not over 15% water, and preferably, as little unsulfonated hydrocarbon material as possible. A convenient amount of such material, for instance, a thousand pounds, is neutralized with a diamyl diamine previously described, so that the resultant compound indicates neutral or slightly basic to methyl orange. or some other acceptable indicator.

It may be well to point out that hydrophile non-hydrophobepetroleum sulphonic acid or acids of the green acid type vary somewhat; for instance, the molecular weight may vary within the range of 350–500 or thereabouts. Naturally these petroleum sulphonic acids may carry some polymerized olefines, free hydrocarbons, or the like, or may even carry a bit of naphthenic acids which represent carboxylated non-sulphonated petroleum acids. As previously stated, these materials are well known commercial products, and are available in the open market, either in the form of the acid itself, or in the form of a salt.

In the claims the amine or, more specifically, the diamine, is referred to as basic to indicate that the basicity is in the neighborhood of that of ammonia, triethanolamine, or amylamine. In some instances the basicity may be somewhat greater, in fact, perhaps considerably greater, and in some instances perhaps slightly less. In order to insure such basicity, it is necessary that there be no aryl or aromatic radical attached to the amino nitrogen atom from which the diamine is produced. In other words, such materials as phenyl amylamine, diphenylamine, phenyl octylamine, etc., are not satisfactory, due to the presence of the aromatic phenyl radical or an aryl radical, such as the naphthyl radical attached directly to the amino nitrogen atom. In the event that such aryl radical is attached to the amino nitrogen atom, the basicity of the amine is reduced to that of the aniline, or the like. Such amines of low basicity do not form stable salts with the petroleum acids of the kind described. For this reason the expression basic is employed to clearly characterize the amine. The term "sulphonic acid" used in the claims is intended to refer to a substance consisting either of a single acid or a mixture of acids.

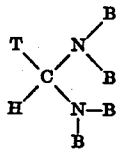
In my divisional application Serial No. 300,843, filed October 23, 1939, I have described a novel process for resolving or breaking petroleum emulsions of the water-in-oil type. Said process involves subjecting the emulsion to the action of a demulsifier consisting of the above described new material or composition of matter. Said material is used either alone or in admixture with another or with other conventional demulsifying agents, and its method of use is the same as that generally employed in resolving or breaking petroleum emulsions of the water-in-oil type with a chemical demulsifier. Briefly stated, the conventional method of using a chemical demulsifier to break a petroleum emulsion consists in introducing the demulsifier into the well in which the emulsion is produced; introducing the demulsifier into a conduit through which the emulsion is flowing; or introducing the demulsifier into a tank in which the emulsion is stored. After treatment the emulsion is allowed to stand in a quiescent state, usually in a settling tank, and usually at a temperature varying from atmospheric temperature to about 200° F., so as to permit the water or brine to separate from the oil, it being preferable to keep the temperature low enough to prevent the volatilization of valuable constituents of the oil. The amount of demulsifier that may be required to break the emulsion may vary from 1 part of demulsifier to 500 parts

of emulsion, up to 1 part of demulsifier to 20,000 or even 30,000 parts of emulsion.

I desire to point out that the superiority of the reagent or demulsifying agent herein described is based upon its ability to treat certain emulsions more advantageously and at a somewhat lower cost than is possible with other available demulsifiers, or conventional mixtures thereof. It is believed that the particular demulsifying agent or treating agent herein described will find comparatively limited application, so far as the majority of oil field emulsions are concerned; but I have found that such a demulsifying agent has commercial value, as it will economically break or resolve oil field emulsions in a number of cases which cannot be treated as easily or at so low a cost with the demulsifying agents heretofore available.

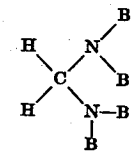
Having thus described my invention, what I claim as new and desire to secure by Letters Patent is:

1. A new compound, consisting of a water-insoluble salt of a basic, methylene diamine of the formula type:



in which T is selected from the class consisting of hydrogen atoms, hydroxy alkyl and aliphatic hydrocarbon radicals, and B is selected from the class consisting of aliphatically-bound hydrocarbon radicals, alicyclic hydrocarbon radicals, aliphatic hydrocarbon radicals interrupted at least once by an oxygen atom, aliphatically-bound hydroxy hydrocarbon radicals and hydroxy alicyclic radicals; said diamine salt being obtained from water-soluble, non-hydrophobe petroleum sulphonic acid of the green acid type.

2. A new compound consisting of a water-insoluble salt of a basic, methylene diamine of the formula type:



in which B is selected from the class consisting of aliphatically-bound hydrocarbon radicals, alicyclic hydrocarbon radicals, aliphatic hydrocarbon radicals interrupted at least once by an oxygen atom, aliphatically-bound hydroxy hydrocarbon radicals and hydroxy alicyclic radicals; said diamine salt being obtained from water-soluble, non-hydrophobe petroleum sulphonic acid of the green acid type.

MELVIN DE GROOTE.