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OVERBASING MANGANESE COMPOUNDS WITH PROMOTERS AND COPROMOTERS

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ABSTRACT OF THE DISCLOSURE

Certain compounds containing acid functions are overbased with manganese by carbonating a system containing the acid, a promoter and a copromoter. Among the acids contemplated are tall oil, sulfonic acids and carboxylic acids such as naphthenic acid.

Organic fluid compositions, as those from lubricants and liquid hydrocarbon fuels, containing the overbased products have improved properties. As examples, the products act to improve combustion and as smoke suppressants in residual fuels, and also to provide detergency properties to lubricating oils.

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a process for overbasing acidic compounds and to lubricant and liquid hydrocarbon fuel compositions containing same. In particular, the invention is concerned with manganese overbasing of acidic materials by carbonation in the presence of a promoter and a copromoter and the use of the product of such process in the indicated media.

Discussion of the Prior Art

The state of the art of overbasing tallates, naphthenates, sulfonates and phenates by alkaline earth oxides is extensive and well developed. The prior art teaches that in general only one promoter is required to achieve overbasing with such alkaline earth metal oxides in the carbonation process. For example, Canadian Pat. No. 801,084 teaches that the extent of overbasing of certain materials in the carbonation process with magnesium oxide is fairly large when a single promoter such as ethylenediamine is present in the system. See also U.S. 3,492,230 containing similar disclosure.

On the other hand, it has now been found that in overbasing the same compounds with manganous oxide in the carbonation process, using a different promoter, the system must include not only such promoter, but also a copromoter to achieve a highly overbased product.

SUMMARY OF THE INVENTION

In accordance with the invention, there is provided a process for preparing an overbased compound of the group consisting of sulfonates and carboxylates which comprises carbonating a dispersion comprising (1) manganous oxide, (2) a member of the group consisting of an organic sulfonic acid and an organic carboxylic acid, (3) a promoter selected from the group consisting of ammonium halides, ammonium nitrate, mono-, di- and trialkyl amine hydrohalides, ammonium sulfide and ammonium peroxydisulfate, and (4) a metal halide copromoter.

Also provided are organic fluid compositions comprising a major proportion of such organic fluid and an amount sufficient to impart improved combustion, smoke suppressant and detergency properties thereto of the product produced in accordance with the method of this invention. The fluids particularly include lubricating oils and liquid hydrocarbon fuels.

DESCRIPTION OF SPECIFIC EMBODIMENTS

In general the overbased, preferably oil-soluble compound is prepared by carbonating a dispersion of a dispersant (i.e., sulfonate or carboxylate), a monohydric or dihydric alcohol, an inert organic solvent therefor, manganous oxide, a promoter and a copromoter.

The sulfonate dispersants useful in the practice of this invention are preferably the oil-soluble petroleum sulfonates, alkyl sulfonic acids, aryl sulfonic acids and alkaryl sulfonic acids. Illustrative are the petroleum sulfonates having a molecular weight of up to about 800, dilauryl aryl sulfonic acid, laurylcetyl aryl sulfonic acid, where aryl includes phenyl, naphthyl and anthracyl, paraffin wax-substituted benzene sulfonic acid (the wax may be obtained from various crude petroleum oil sources and will average about 24 carbon atoms), polyolefin alkylated benzene sulfonic acid, such as polypropyl benzene sulfonic acid where the polypropyl has up to about 30 carbon atoms, dialkyl benzene sulfonic acids, naphthalene sulfonic acid and the alkyl-substituted naphthalene sulfonic acids, where the alkyl has from about C_6 to about C_{30} carbon atoms, preferably from about 12 to about 24 carbon atoms.

Normally, the alkyl sulfonates require about 24 carbon atoms for oil solubility. The alkylating agent may, of course, have a chain length of about 24 carbon atoms, or it may be a mixture of agents whose average chain length is about 24 carbon atoms. The alkaryl sulfonates, on the other hand, require for solubility an alkyl portion totaling at least about 18 carbon atoms. Here again, these can be straight C_{18} or mixtures of agents which average about 18 carbon atoms.

The carboxylate dispersant should preferably be substantially oil-soluble, both as the free acid and as the manganese salt. Thus, acids should have a hydrocarbyl of at least about 7 carbon atoms and usually not more than 30 carbon atoms. Preferably the carboxylates will have from about 8 to about 30 carbon atoms, and the parent acid may be mono- or dibasic. "Hydrocarbyl" as used herein means an organic radical of carbon and hydrogen which may be aliphatic, alicyclic, aromatic or combinations of these. Such radicals may be saturated or aliphatically unsaturated. Illustrative, non-limiting examples of the useful acids are tall oil, oleic acid, naphthenic acid, lauric acid, stearic acid, linoleic acid, palmitic acid, enanthic acid, arachidic and behenic acids, polyisobutyl succinic acid and the like. Also included are aromatic carboxylic acids, such as alkyl-substituted benzoic, salicylic and phthalic, where the alkyl group or groups are attached to the aryl nucleus of the acid and contain a total of at least 7 carbon atoms as stated above. Examples are diamyl benzoic acid, octadecyl benzoic acid and the like.

Tall oil is defined in Kirk-Othmer's "Encyclopedia of Chemical Technology," vol. 19, p. 614 as a mixture of rosin and fatty acids together with unsaponifiables. The chemical is obtained by acidifying the rosin and fatty acid sodium soaps recovered from the concentrated black liquor in the Kraft or sulfate pulping process.

The contemplated naphthenic acids are monocarboxylic acids of the naphthene (alicyclic) series of hydrocarbons. Their general formula may be written as $R(CH_2)_nCOOH$, where R is a cyclic nucleus composed of one or more rings. The rings are usually five-membered, preferably alkylated so that the total carbon chain length will fall within the above-stated range.

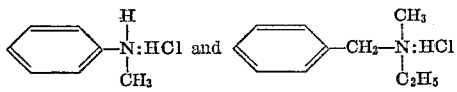
The alcohols which may be employed include monohydric alcohols having from 1 to about 18 carbon atoms, such as methanol, ethanol, butanol and the like. Also included are the lower alkoxy alcohols such as methoxyethanol. Of the alcohols included, methanol is preferred. Dihydric alcohols such as ethylene glycol, diethylene glycol and propylene glycol may be used.

The inert organic solvent may be aromatic or aliphatic, i.e., it may be selected from such materials as benzene, toluene, xylene, chlorobenzene, 1,2-dichlorobenzene, the hexanes, petroleum ether, kerosene and a process oil.

The carbonation may be carried out at temperatures ranging from about 50° C. to about 200° C. Preferably, the temperature range will be within the range of about 25° C. to about 125° C. For example, when using methanol as the alcohol, carbonation is preferably carried out from about 50° C. to about 65° C. The alkoxyalkanols may require a higher temperature, e.g., from about 80° C. to about 95° C. when using 2-methoxyethanol.

As has already been made apparent, overbasing with manganous oxide does not occur in the presence of the herein dislosed promoters alone, nor in the presence alone of substances referred to herein as copromoters, As the copromoter, the alkaline earth halides are generally applicable. These include calcium chloride, barium chloride and magnesium chloride, as well as other salts of alkaline earth metal and halides such as bromine or iodine. Also applicable are the halides of other metals, such as $AlCl_3$ and $FeCl_3$.

The ammonium halides appear to cooperate with the metal halides to give highly overbased products, and this seems to be true also of the mono-, di- and trialkylamine hydrohalides, the alkyl group containing from 1 to about 18 carbonatoms, as for example the hydrohalides of trimethyl-, trioctyl-, tridecyl- and trioctadecylamine, the mono-, di- and trialkarylamine hydrohalides, and the mixed aryl-alkyl amine hydrohalides having from about 7 to about 30 carbon atoms. These would include the hydrohalides of tritolyl-, trioctadecylphenylamine and the like, as well as those of the type



However, ammonium compounds containing sulfur are unpredictable in their action, compounds like ammonium sulfide $[(NH_4)_2S]$ and ammonium peroxydisulfate

$$[(NH_4)_2S_2O_8]$$

being useful, as opposed to the inactive ammonium sulfate $[(NH_4)_2SO_4]$. Furthermore, such other compounds as the tetraalkyl ammonium halides or tetraalkarylammonium halides are not promoters when used with the alkaline earth metal halides.

It is contemplated that the promoters and copromoters will be effective when the respective concentrations thereof are selected from the range of from about 0.1% to about 20% by weight of the manganous oxide employed. Preferably each component will be present in a concentration of from about 2% to about 10% by weight of MnO. It will be understood that the concentrations of the two components may be, but may not necessarily be, the same.

The manganous oxide used in this invention is available in several grades containing varying amounts of manganese, i.e., it is of varying purity. There is a so-called special or electronics grade of MnO of about 98% purity. This product can be used directly without any pretreatment. Another grade is referred to as "60% Mn regular" by one manufacturer and contains about 78% MnO. When this latter grade is used directly in the process of this invention, the higher degree of overbasing cannot always be expected.

However, MnO of lower quality can be used if subjected to a pretreatment step. This may be done in at least two ways, one of which involves heating dispersant (i.e., the sulfonic or carboxylic acid) and MnO together for from about 1 to about 20 hours at about 100° C. to about 200° C., preferably from about 150° C. to about 200° C., and then proceeding in the disclosed manner to form the overbased product. Another way is to heat MnO, promoter and copromoter together for several hours at from about 100° C. to about 200° C. prior to forming the overbased product as taught herein. The following will illustrate this aspect of the disclosure.

A dispersion of 40.8 parts of "60% Mn" manganese oxide, 100 parts of a mixture of C_5–C_9 carboxylic acids and lactones having an acid number of 250.8, 500 cc. toluene, 125 cc. 2-methoxyethanol, 1.0 part of ammonium chloride and 2.0 parts of calcium chloride was carbonated at 90° C. for about 7.5 hours. Because of high recovery of unreacted material, the product was not isolated.

Then 100.0 parts of "60% Mn" and 100 parts of the same acid were heated under vacuum at 200° C. for 5½ hours. This pretreated mixture was then carbonated in the presence of xylene, 2-methoxyethanol, 2 parts of

$$NH_4Cl$$

and 4 parts of $CaCl_2$ at 90° C. for 24 hours. There was a high recovery of product and a correspondingly low recovery of unreacted solids. The percent of manganese overbasing was 289.

Generally, the amount of manganous oxide used will depend upon the amount of overbasing desired. Thus, for an overbased product, more MnO will be required than an amount equivalent to the quantity of dispersant present in the reaction mixture. At the lower degrees of overbasing, where the reaction is fairly rapid, it will usually not be necessary to use an excess. However, as the degree of overbasing is increased, it may become necessary to use a slight excess, say on the order of 10%, of the MnO to drive the reaction to the degree desired in a reasonable time. Of course, after the maximum overbasing for a given system has been reached, i.e., no further overbasing can be obtained, the amount of excess used should not be more than required to achieve reaction in the shortest time.

Having described the invention in general terms, the following is offered as illustrative of the process of the invention and of the usefulness of the products therefrom as lubricant or hydrocarbon fuel additives.

A dispersion of 100 parts of Pamak 25–A Tall Oil, 24.0 parts of MnO of 98% purity, 5.0 parts of NH_4Cl, no copromoter, 500 cc. of monochlorobenzene (MCB and 125 cc. of 2-methoxyethanol (ME) was carbonated at 90° C. for 7.5 hours using an excess of CO_2 over that required for reaction. Thereafter, 200 g. of Promor #5 process oil was added and the mixture was heated under reduced pressure to remove monochlorobenzene and 2-methoxyethanol.

Table 1 shows the results using the above-specified acid (Item 1) as well as the results for other acids with the same MnO, overbased in accordance with the invention substantially as herein described. All results in the table were obtained by carbonating the mixtures shown at temperatures of from about 80–95° C., and from less than 2 hours to about 8 hours.

TABLE 1

Item	Dispersant (wt. g.)	MnO (g.)	Solvent (cc.)	Alcohol (cc.)	Promoter (wt., g.)	Copromoter (wt., g.)	Percent Mn overbasing
1	Tall oil (100) [1]	24	MCB (500)	ME (125)	NH_4Cl (5.0)		0.0
2	do [1]	24	MCB (500)	ME (125)		$CaCl_2$ (5.0)	0.0
3	do [1]	24	MCB (500)	ME (125)	NH_4Cl (1.0)	$CaCl_2$ (2.0)	81.0
4	do [2]	30	MCB (500)	ME (125)	NH_4Cl (1.0)	$CaCl_2$ (2.0)	163.8
5	do [2]	40	MCB (500)	ME (125)	NH_4Cl (1.0)	$CaCl_2$ (2.0)	192.0
6	do [2]	40	MCB (500)	ME (125)	NH_4Cl (2.0)	$CaCl_2$ (4.0)	228.0
7	do [1]	84	Xylene (500)	MeOH (200)	NH_4Cl (4.0)	$CaCl_2$ (8.0)	296.0
8	do [2]	50	MCB (500)	ME (225)	NH_4Cl (2.0)	$CaCl_2$ (4.0)	318.0
9	Naphthenic acid (100) [3]	45	Kerosene (500 g.)	2-Pr (150) [6]	NH_4Cl (2.0)	$CaCl_2$ (4.0)	224.0
10	Sulfonic acid (200) [4]	34.6	Toluene (500)	ME (150)	NH_4Cl (1.0)	$CaCl_2$ (2.0)	180.0
11	U.C. acids (100) [5]	63.4	Kerosene (500 g.)	2-Pr (200)	NH_4Cl (1.0)	$CaCl_2$ (2.0)	177.3
12	Tall oil (100.) [2]	20.4	Xylene (500)	ME (125)	NH_4Br (1.0)	$CaCl_2$ (2.0)	91.2
13	do [2]	20.4	do	ME (125)	NH_4NO_3 (1.0)	$CaCl_2$ (2.0)	94.2
14	do [2]	20.4	do	ME (125)	$(NH_4)_2S_2O_8$ (1.0)	$CaCl_2$ (2.0)	94.2
15	do [2]	20.4	do	ME (125)	$(NH_4)_2S$ (1.0)	$CaCl_2$ (2.0)	100

[1] Acid No. 187—Sold by Hercules Powder Company as Pamak 25-A.
[2] Acid No. 158.1-161.0—Sold by Union Camp Corporation as Unitol "S".
[3] Acid No. 178.
[4] Cracked wax benzene sulfonic acid having an acid no of 68.44.
[5] Mixture of C_5-C_9 carboxylic acids and lactones having an acid no. of 250.8.
[6] 2-propanol.

It is clear from the above table that when either the promoter or copromoter is absent, there is no manganese overbasing. Furthermore, it is apparent that when a variety of promoters are used with the alkaline earth metal halide calcium chloride, there is always a considerable degree of overbasing with very excellent results in several of the instances indicated. For example, the eighth item in the table shows a product overbased to the extent of 318%. The term "overbased" means that the product contains more metal than can be accounted for on the basis of the neutral material. Broadly, therefore, the overbased dispersants of this invention can be defined as a product containing more equivalents of metal than the equivalents based on the combining weight of the dispersant.

It was stated above that certain ammonium compounds will not function with alkaline earth metal halides as promoters. Included among these were indicated to be such compounds as $(NH_4)_2B_{10}O_{16}\cdot 8H_2O$ and $(NH_4)_2SO_4$. Even those which do function as promoters with the alkaline earth metal halides will not operate with certain other alkaline earth metal compounds. For example, no overbasing was obtained when NH_4NO_3 was combined with $Ca(NO_3)_2$.

UTILITY OF PRODUCTS

The products produced by the novel process are useful as combustion improvers and smoke suppressants in residual fuels and as lube oil and liquid hydrocarbon fuel detergents.

SMOKE SUPPRESSANT IN RESIDUAL FUELS

The smoke suppressant test was similar to the Bacharach Oil burner test as described in Bulletin 111B of the Bacharach Instrument Company. Instead of comparing the amount of sooting on the Bacharach Oil Burner Smoke Scale, as directed in the bulletin, the amount of actual carbon pick-up on the filter paper was determined. This was done by weighing the filter paper before and after placing it in the flue, the difference in weight found being a measure of the smoking tendancy of the fuel. The burning rate of fuel was adjusted so that the volume of gases which produced the sooting was known. In this way, the quantity of carbon per volume, 10 cubic feet in this case, was calculated.

In this test, a No. 6 residual fuel (A.S.T.M. D-396-62T) was used. It contained the additives as indicated in the following table.

TABLE 2

Additive	Mn conc., p.p.m.	Smoke, carbon, mg/10 cu. ft.	Smoke reduction, percent	Nozzle: Oil temp., °F.	Nozzle: Air press., in. hg	Fuel rate, #/hr.
Item 8, Table 1	0	26.7		203	18.0	5.50
	10	19.0	28.84	203		5.49
	50	11.7	56.18	205		5.50
	100	7.4	72.3	206		5.50
Item 9, Table 1	0	25.4		203	18.0	5.50
	10	19.4	23.1	203	18.0	5.49
	50	9.9	61.02	207	18.0	5.50
	100	8.0	68.5	204	18.0	5.50
Item 10, Table 1	0	100.0		203	18.0	5.50
	10	30.0	26.8	205	18.0	5.50
	50	18.9	53.9	206	18.0	5.50
	100	13.0	68.3	207	18.0	5.51
Item 11, Table 1	0	20.3		204	18.0	5.51
	10	19.5	3.94	205	18.0	5.48
	50	11.2	44.32	206	18.0	5.48
	100	6.5	68.0	204	18.0	5.48

SULFURIC ACID NEUTRALIZATION TEST

This method gives a measure of the ability of detergent additives to neutralize strong acids formed in engines operating on sulfur containing fuels. H_2SO_4 is mixed with a heated blend of the additive and the oil. A solution of this is formed in isooctane which is then centrifuged to separate insolubles. The optical density of the clear solution is then measured. From this value the optical density of the original additive blend diluted to a corresponding amount with isooctane is subtracted. The difference gives the optical density of the dispersed H_2SO_4 reaction products. The optical density of an acetone extraction of the isooctane-oil solution is then determined. The average optical density of the oil-isooctane solution is expressed as the optical density of the dispersed H_2SO_4 reaction product. The average density of the acetone solution is expressed as the optical density of the non-dispersed H_2SO_4 reaction products. The total of these values or

either one alone is used in the evaluation of detergent additives.

PYRUVIC ACID DISPERSION TEST

This method gives a measure of the dispersant value of additives and serves to predict the performance of detergent additives in engines operating on low sulfur content fuels. When used in combination with the neutralization of H_2SO_4 bench test procedures its serves to predict the performance of detergent additives in engines operating on high sulfur content fuels. Pyruvic acid is mixed with a heated blend of the additive and the oil. The mixture is diluted with benzene and centrifuged to separate insolubles. The insolubles are dissolved in acetone. The optical density of the oil-benzene solution gives the total amount of color. From this value the optical density of the initial additive blend diluted with benzene to a corresponding amount is subtracted. This corrected value is expressed as the optical density of the dispersed pyruvic acid polymer. The optical density of the acetone solution is expressed as the optical density of the non-dispersed pyruvic acid polymer. These values are used in the evaluation of the detergent additives.

Table 3 summarizes the results obtained. In the ratings given, the higher the percentage obtained in the Pyruvic Acid Test, the better the additive; a lower result with sulfuric acid denotes the better additive.

TABLE 3

[Blend of 3% active ingredient and 1% corrosion inhibitor [a] in a base oil [b]]

Item	Pyruvic acid, percent	Sulfuric acid
1—(containing only the corrosion inhibitor)	79.3	0.194
2—Item 8, Table 1	95.8	0.108
2—Item 10, Table 1	96.2	0.119

[a] 1,3-dimethylbutyl zinc dithiophosphate.
[b] S.A.E. 30 grade mineral oil, S.U.V. at 210° F. of 64.1.

Oils which may be improved include mineral oils, both paraffinic and naphthenic, synthetic fluids, and greases made therefrom. The mineral and synthetic oils may or may not be of lubricating viscosity. The synthetic fluids may be synthetic hydrocarbons such as those produced by polymerizing an olefin such as decene. These also include the hydrogenated members of such polymers. Further classes of synthetic fluids include the polysiloxanes, the polyalkylene glycols and polymers of olefin oxides. Of especial interest are synthetic esters made from polycarboxylic acids and monohydric alcohols or from polyhydric alcohols and monocarboxylic acids. Synthetic esters of the latter type (i.e., using polyhydric alcohols and monoacids) are becoming increasingly important in the lubrication of jet engines. Among those showing promise in this area are esters made by reacting such polyhydric alcohols as the trimethylol alkanes, the pentaerythritols, including mono-, di- and tripentaerythritol, with a monocarboxylic acid containing from about 4 to about 10 carbon atoms, preefrably from about 5 to about 9 carbon atoms. Also mixtures of such acids may be used to prepare the esters.

The hydrocarbon fuels useful in the practice of this invention include those specified as Nos. 4 to 6 in Table 1 of ASTM D-396-62T.

It will be observed that no attempt has been made to describe the products as to their true makeup. Applicants do not known what precise products are obtained, so the description and the claims are limited to such compounds as reaction products.

Although the present invention has been described with certain specific embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of this invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the appended claims.

We claim:

1. A process for preparing an overbased compound of the group consisting of sulfonates and carboxylates, which comprises carbonating, at a temperature of from 50° to about 200° C. until the reaction is complete, a dispersion comprising (1) excess manganous oxide, (2) a member of the group consisting of an oil soluble organic sulfonic acid and an oil soluble organic carboxylic acid, (3) a promoter selected from the group consisting of ammonium halides, ammonium nitrate, mono-, di- and trihydrocarbyl-amine hydrohalides containing 1 to 30 carbon atoms, ammonium sulfide and ammonium peroxysulfate and (4) a metal halide copromoter selected from the group consisting of alkaline earth metal halides, aluminum trichloride and ferric chloride, wherein the proportion of promoter and copromoter is from about 0.1% to about 20% by weight based on the weight of the manganous oxide.

2. The process of claim **1** wherein the organic sulfonic acid is a member of the group consisting of oil-soluble petroleum sulfonic acids, alkyl sulfonic acids, aryl sulfonic acids and alkaryl sulfonic acids.

3. The process of claim **2** wherein the alkyl sulfonic acid has a minimum of 24 carbon atoms in the alkyl portion.

4. The process of claim **2** wherein the alkaryl sulfonic acid has a minimum of 18 carbon atoms in the alkyl portion.

5. The process of claim **1** wherein the organic carboxylic acid is one having from about 7 to about 30 carbon atoms.

6. The process of claim **5** wherein the acid is selected from the group consisting of tall oil, oleic acid, naphthenic acid, lauric acid, stearic acid, linoleic acid, palmitic acid, enanthic acid, arachidic acid, behenic acid and polyisobutyl succinic acid.

7. The process of claim **1** wherein there is also present in the dispersion an alcohol having from 1 to about 18 carbon atoms.

8. The process of claim **1** wherein the said hydrocarbylamine hydrohalides are selected from the group consisting of mono-, di- and trialkylamine hydrohalides, mono-, di- and trialkanylamine hydrohalides and the mixed alkylarylamine hydrohalides.

9. The process of claim **8** wherein the trialkylamine hydrohalides, the alkyl portion contains from 1 to about 18 carbon atoms.

10. The process of claim **8**, wherein in the trialkarylamine and mixed alkyl-aryl amine hydrohalides, the total number of carbon atoms is from about 7 to about 30 carbon atoms.

11. The process of claim **1** wherein the promoter is ammonium chloride.

12. The process of claim **1** wherein the copromoter is calcium chloride.

13. The process of claim **1** wherein, prior to carbonation, the MnO is subjected to a pretreatment step.

14. The process of claim **13** wherein said pretreatment step comprises heating MnO and dispersant together at a temperature of from about 100° C. to about 200° C.

15. The process of claim **13** wherein said pretreatment step comprises heating MnO, promoter and copromoter together at from about 100° C. to about 200° C.

16. A lubricant or hydrocarbon fuel composition comprising a major proportion of a lubricant or hydrocarbon fuel and a detergency amount of a product obtained by carbonating, at a temperature of from 50° to about 200° C. until the reaction is complete, a dispersion of (1) excess manganous oxide, (2) a member of the group consisting of an oil soluble organic sulfonic acid and an oil soluble organic carboxylic acid (3) a promoter selected from the group consisting of ammonium halides, ammonium nitrate, mono-, di- and trihydrocarbylamine hydrohalides containing 1 to 30 carbon atoms, ammonium sulfide and ammonium peroxydisulfate and (4) a metal halide copromoter selected from the group consisting of alkaline earth metal halides, aluminum trichloride and

ferric chloride wherein the proportion of promoter and copromoter is from about 0.1 to about 20% by weight based on the weight of the manganous oxide.

17. The composition of claim **16** wherein the organic sulfonic acid is a member of the group consisting of oil-soluble petroleum sulfonic acids, alkyl sulfonic acids, aryl sulfonic acids and alkaryl sulfonic acids.

18. The composition of claim **17** wherein the alkyl sulfonic acid has a minimum of 24 carbon atoms in the alkyl portion.

19. The composition of claim **17** wherein the alkaryl sulfonic acid has a minimum of 18 carbon atoms in the alkyl portion.

20. The composition of claim **16** wherein the organic carboxylic acid is one having from about 7 to about 30 carbon atoms.

21. The composition of claim **20** wherein the acid is selected from the group consisting of tall oil, olenic acid, naphthenic acid, lauric acid, stearic acid, linoleic acid, palmitic acid, enanthic acid, arachidic acid, behenic acid and polyisobutyl succinic acid.

22. The composition of claim **16** wherein there is also present in the dispersion an alcohol having from 1 to about 18 carbon atoms.

23. The composition of claim **16** wherein the said hydrocarbylamine halides are selected from the group consisting of mono-, di- and trialkylamine hydrohalides, mono-, di- and trialkarylamine hydrohalides and the mixed alkyl-arylamine hydrohalides.

24. The composition of claim **23** wherein in the trialkylamine hydrohalides, the alkyl portion contains from 1 to about 18 carbon atoms.

25. The composition of claim **23** wherein in the trialkarylamine and mixed alkyl-aryl amine hydrohalides, the total number of carbon atoms is from about 7 to about 30 carbon atoms.

26. The composition of claim **16** wherein the promoter is ammonium chloride.

27. The composition of claim **16** wherein the copromoter is calcium chloride.

28. An overbased product produced by a process comprising carbonating, at a temperature of from 50° to about 200° C. until the reaction is complete, a dispersion of (1) excess manganous oxide, (2) a member of the group consisting of an oil soluble organic sulfonic acid and an oil soluble organic carboxylic acid, (3) a promoter selected from the group consisting of ammonium halides, ammonium nitrate, mono-, di- and trihydrocarbyl-amine hydrohalides containing 1 to 30 carbon atoms, ammonium sulfide and ammonium peroxydisulfate and (4) a metal halide copromoter selected from the group consisting of alkaline earth metal halides, aluminum trichloride and ferric chloride wherein the proportion of the promoter and copromoter is from about 0.1 to about 20% by weight based on the weight of the manganous oxide.

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