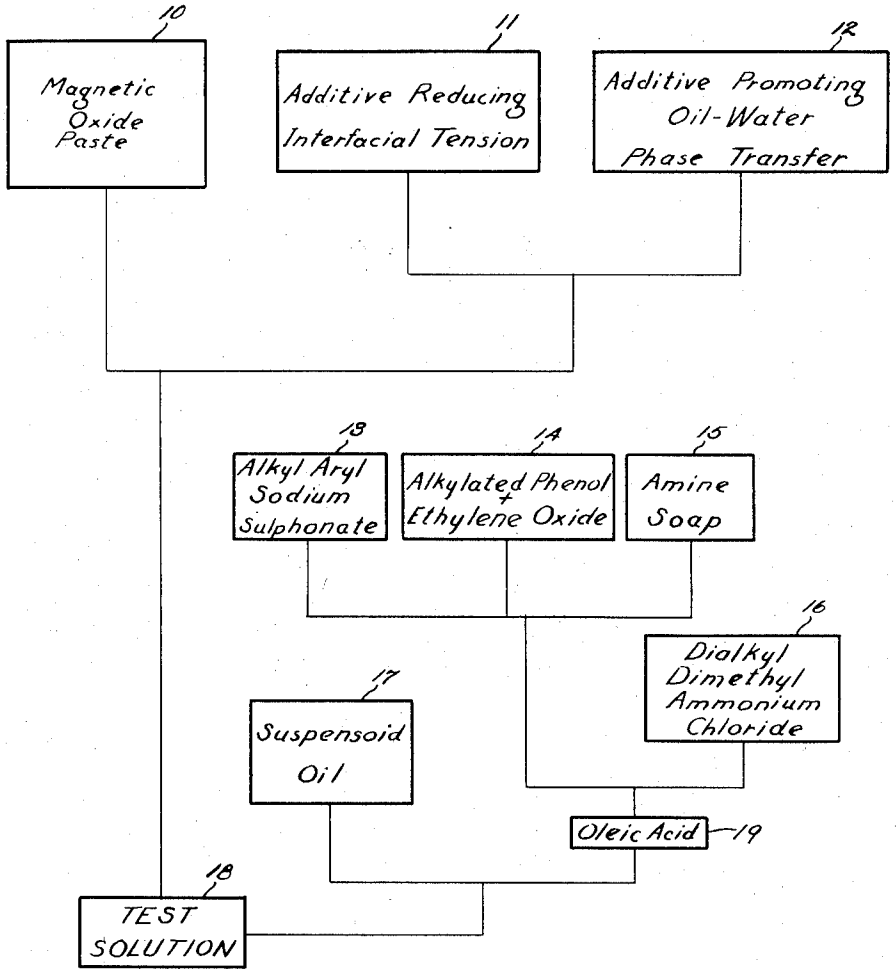
Oct. 26, 1965 R. G. HANNEMAN 3,214,378

COMPOSITION FOR MAGNETIC PARTICLE TESTING

Filed Sept. 1, 1960



INVENTOR.
ROBERT GORDEN HANNEMAN
BY
Myer, Baldwin, Doran & Young
ATTORNEYS

United States Patent Office 3,214,378 Patented Oct. 26, 1965

3,214,378

COMPOSITION FOR MAGNETIC PARTICLE TESTING

Robert Gorden Hanneman, Newbury, Ohio, assignor to The R.G.H. Company, Inc., Cleveland, Ohio, a corporation of Ohio

Filed Sept. 1, 1960, Ser. No. 53,468
1 Claim. (Cl. 252—62.5)

The present application is a continuation-in-part of my copending application Serial No. 502,967, filed April 21, 1955, now abandoned.

This invention relates to a method and compositions for magnetic particle testing.

The presently accepted method for magnetic particle testing is set forth in the Report of the Iron and Steel Division of the Society of Automotive Engineers, adopted January 1941 and revised January 1942. Also see, Military Specification, Inspection Process, Magnetic Particles, MIL–I–6868A, Nov. 6, 1952. As usually practiced, a fine magnetic oxide dispersed in an oily medium is mixed with a light oil to make an inspection. This oxide dispersed in the oily medium is commonly known as No. 7 Black Paste or sometimes by the proprietary name "Magnaflux" paste. The recommended suspensoid is a petroleum distillate of 46 degrees Baumé and 41 seconds viscosity (Saybolt) or a maximum of 5.0 centistokes. In the absence of an oil of this character, kerosene is a satisfactory substitute. There is a trend in the aircraft industry to use a lighter suspensoid such as Stoddard solvent. The paste is suspended in the light oil to amount of 1 or 2 percent solids in the oil. This vehicle or oil bearing the magnetic substance is sprayed or poured over the test piece while the latter is subjected to a suitable direct current of electricity or magnetic field.

A disadvantage of the presently used method is that the oil and grinding assistants in the paste when diluted with the vehicle and spread over the test piece will not evaporate clean and residues are left on the tested specimen which oxidize to a gum. This condition is aggravated by the action of the iron oxide particles to the point where it is almost impossible to remove the residue of the testing process without mechanically scrubbing the specimen in the presence of very strong cleaners. Also, as the suspensoid oil becomes "used," particles tend to agglomerate in the machine causing the efficiency to drop and causing the machine to plug up so that periodic shut downs occur.

A greater problem than the removal of the above described formation of gum is the removal of the iron oxide particles from the test specimens which have been pressed to the surface by the magnetic force applied thereto as a part of the testing and the resulting rust and corrosion from these particles being in intimate contact with the specimens. In the present invention, the removal of an iron oxide particle with a protective hydrophilic/lipophobic jacket and yet the particle is kept from flocculating with other particles. This jacket can then be removed by water or other solvents which destroys the bond holding the particle to the test piece.

Therefore, the present invention provides a means of removal of the iron oxide particles after testing as well as a means of easily removing the gum formation on the test piece surface.

An object of the present invention is to improve the process of magnetic particle testing so that the tested specimen is readily washed clean after the testing process is concluded. This consists in treating the magnetic oxide with an additive which reduces the interfacial tension of oil against water to a very low degree (approximately 2 dynes per centimeter) and to assist in reducing later oxi-

dation effects; plus an additive for promoting the oil-water phase transfer and to assist in the oil dispersion; plus a protective colloid to supply a water soluble film or insulating means between the particles of magnetic iron oxide and the part being tested.

A second main step in the method is the treatment of the suspensoid with additives to lower the surface tension and to aid in emulsification when the specimen is washed after testing and to assist in suspending particles while testing and to permit a large amount of water to be added without flocculations of magnetic oxide or effecting the testing procedures.

As a third step, the pre-treated magnetic oxide paste and the pre-treated suspensoid oil are then mixed together in the proper proportions to make my improved test solution.

A fourth main step in the method, when water is to be used as a cleaning means, is the use of a soaking means to displace and absorb oil remaining on the part tested as well as on the particles, and to replace it with a water soluble soap. The part may be placed in the soaking liquid while wet with the suspending oil or it may be preferably allowed to dry. This step permits the part to be rinsed clean with water without additional cleaning compounds or mechanical scrubbing.

The drawing shows in diagrammatic form the various steps involved in forming my improved test solution.

The ingredient which I have numbered 10 on the diagram and called "magnetic oxide paste" may be that which is used in the S.A.E. standard test and known as "No. 7 Black Paste." This material consists of a fine magnetic oxide dispersed in an oily medium which, when mixed with a light oil to make up an inspection bath, shall maintain a satisfactory suspension and must not tend to agglomerate rapidly in suspension. A dispersing agent is incorporated to prevent agglomeration and to disperse the particles in suspension in the oil. The magnetic oxide employed shall consist of at least 85 percent magnetic oxide of iron. The material in paste form shall contain at least 75 percent of solid oxide of iron.

In place of the above, I may take a fine magnetic oxide powder dispersed in oil to a heavy paste consistency and incorporate the ingredient which I have marked 11 on the diagram and indicated there as an "additive reducing interfacial tension."

The ingredient which I have marked 11 on the diagram is indicated there as an "additive reducing interfacial tension." This is a chemical added to reduce the interfacial tension of the oil against the water in the final mixture to a very low degree, preferably, 2 dynes per centimeter or less. This also assists in reducing oxidation which normally causes the test material residue to become a varnish-like gum on the specimen. This ingredient 11 may be a proprietary substance sold by Commercial Solvents Corporation and known as "Alkaterge-C." This I believe to be a substituted oxazoline with an oxazole content of about 70 percent by weight. I may also use, for this ingredient 11, di(2-ethyl hexyl) amine hydrochloride which is sold by Carbide & Carbon Chemicals Company. Sometimes I may omit ingredient 11 where the amines in ingredient 15 are sufficient to reduce the interfacial tension.

The ingredient which I have marked 12 on the diagram is indicated as an "additive promoting oil-water phase transfer." This is an oil-water soluble quarternary ammonium salt to assist the oil-water phase transfer and to assist in the oil dispersion. My tests indicate that ionic and non-ionic wetting agents could be mixed with the oil-wetted magnetic oxide paste, but only certain wetting agents in particular quantities give the desired dispersion in the suspending oils. The preferred salt for this pur-

pose is dialkyl-dimethyl ammonium chloride with the alkyl group having about 8 to 18 carbon atoms.

In making the above additions, I take ten parts of ingredient **12** to one part of ingredient **11** and mix these together completely with 80 or 90 parts of the magnetic oxide and oil paste. The proper combination of materials and mixing time is determined by a resulting stiff consistency following a semifluid state of the material. Also I may add, during the mixing, if desired, a sufficient amount of water soluble cellulose solution as a protective colloid. Such water soluble celluloses are methyl cellulose, carboxy methyl cellulose, carboxy methyl hydroxy ethyl cellulose, and the like.

The mixing time for the ingriedients **10** plus **12** or **10** plus **11** plus **12** was determined by observation of the ease of complete dispersion of the mixture in oil and in water. The point of complete mixing of these ingredients **10**, **11** and **12** was indicated as that point at which the mixture would go into good dispersion in either oil or water quickly. However, in defining the suspension in water, it should be understood that this is not a complete suspension of the individual magnetic oxide particles in the water but the suspension of very small loosely formed groups of particles sized at the same level of particle size as that of the dialkyl-dimethyl ammonium chloride compound when it is added to oil at 60 degrees F. and given the same agitation.

The additions to the suspensoid oil, now to be described, were selected with various considerations in mind. For instance, it was desired to build a soft jacket around the magnetic oxide particle to keep it from being locked to the tested part by the action of the magnetic field during testing, and to have a water soluble layer under the particle before, during and after the suspending oil had dried. The additive to the suspensoid oil was also regarded as a means for keeping the particles de-flocculated and as a means of achieving instant water dispersions whether the particles were still wet with oil or after the particles had dried.

It was felt that certain amides and amide soaps could be used for this "jacket" material, especially those that were non-drying in nature, and it was also felt that glycols might help. However, the problem was complicated by the fact that (a) flocculation must not occur in the suspension; (b) mixture must be stable; (c) particle flow should not be impeded; (d) the iron oxide particle settling rate must be almost the same as for iron oxide particles in plain oil; and (e) the cost must be moderate.

The vegetable gums were considered and tried but it was found that by themselves, they were worthless, but when used with the finally selected mixture, there were some advantages.

From the evidence of my tests, it was indicated that something having very great particle wetting or dispersive qualities was needed as well as a material to maintain the desired de-flocculation, and a material that would readily allow wetting by oil or water. Tests using various wetting and dispersing agents indicated to me that a balanced combination of anionic, nonionic, cationic materials with the proper hydrophilic/lipophobic characteristics would be needed. I have found out that the combination of ingredients **13**, **14** and **15** as subsequently disclosed herein, was the wetting agent desired and ingredient **16** would take care of the de-flocculation. The right amount of ingredients **13** plus **14** plus **15** on the one hand and of ingredient **16** on the other was determined by observing the reaction of these ingredients in the presence of suspensoid oil. The balance point was selected as that which (a) did not cloud the mixture; (b) did not increase the viscosity; and (c) did not cause granulation salting out or instability. This proper ratio is hereinafter disclosed.

The additions to the suspensoid oil are made in several different steps. The ingredient which I have marked **13** on the diagram is indicated as "alkyl aryl sodium sulfonate."

The ingredient indicated on the diagram as **14** is there marked "alkylated phenol+ethylene oxide." This is actually a reaction product of the alkylated phenol plus ethylene oxide. The preferred products for ingredient **14** are alkyl phenoxyl polyoxyethylene ethanol or alkyl aryl polyether alcohol.

The ingredient indicated at **15** on the diagram is there designated "amine soap." This is an additive for lowering the surface tension and for promoting emulsification. For this ingredient **15** I may use a reaction product of triethanolamine and lauric or oleic. For this ingredient **15** I may also use the reaction product between potassium hydroxide and oleic or lauric acid.

The ingredients **13**, **14** and **15** are taken in approximately equal amounts, or I have had good results using the proportions of 2 parts of **13** to one part of **14** to 2 parts of **15**. In either case, the ingredients **13**, **14** and **15** are mixed and caused to combine and react at a temperature 174 degrees F. or slightly higher, and allowed to precipitate or settle and the precipitate discarded.

For ingredient **16**, I use the same ingredient as indicated at **12**. This as mentioned before is dialkl dimethyl ammonium chloride. I take 57 to 59 percent of ingredients **13** plus **14** plus **15** reacted together, and combine them with 43 to 41 percent of ingredient **16** at approximately 120 degrees F.

Preferably, but not necessarily, I next add sufficient higher fatty acid such as oleic acid or lauric acid to lower the pH of the mixture to 6.5.

The suspensoid oil indicated as ingredient **17** on the diagram may be one of several similar oils. It may be the standard recommended by the S.A.E., namely, on oil of 46 degrees Baumé by American Petroleum Institute Standards, 41 seconds viscosity (Saybolt), 165 degrees F. flash point (Tagliabue Open Cup), distillation having an initial point of 390 degrees F. and end point of 490 degrees F. and color 25 on the Saybolt chromometer. As mentioned previously, it might also be Stoddard solvent. Or it may be a mineral oil such as S.A.E. No. 5 or Sohio Tek No. 15. In any case, I use approximately 97 to 95 percent of the suspensoid oil, ingredient No. **17** on the diagram, and 3 to 5 percent of the additive mixture described above.

The modified suspensoid oil is then thoroughly mixed with the magnetic particles plus their additives **11** and **12** and previously described to make the test solution indicated at **18**. This test solution is then flowed over the specimen to be tested while the specimen is subjected to a direct current of the proper amperage or strong magnetic field.

The tested specimen may then be cleaned in a standard vapor degreaser or further steps of my invention may be utilized to aid in finally cleansing the specimen.

The soaking or cleaning step will next be described. This is the point in my process where one of several methods might be used. For instance, (1) the oil might be incorporated in or become a part of a soap, or (2) the oil might be displaced or emulsified by water and a detergent, or (3) the oil might be coupled with the water by means of an alcohol or other coupling agent, or (4) the oil might be eliminated from the tested piece and the associated magnetic oxide particles by a combination of (1) and (2), or (5) a combination of (1), (2) and (3) mentioned herein. For practical reasons, the 4th solution was selected.

The reasons for this choice were: (a) the cost of the material, (b) the conditions of the suspensoid oil remaining on the tested part are never the same in any two operations since more or less draining and drying time is allowed and this will vary the amount of oil to be replaced or otherwise moved or changed, (c) the single agents mentioned in (1), (2) and (3) above are not quite as good as a slightly unstable combination of these agents

for the accomplishment of the cleaning tasks due to the short cleaning time allowance usually encountered in a production testing operation, and (d) the use of these multiple agents allows selective work to be done, namely, coupling the oil to a detergent and water combination, making a soap with the oil, and replacing and enlarging the particle "jacket" as pre-formed in the testing solution, with a completely water soluble covering. The agent indicated at (1) above for incorporating the oil in a soap, in my preferred form, is oleic acid plus an amine or other powerful emulsifying soap. The agent (2) above for displacing the oil by use of water and a detergent is the ingredients **13** plus **14** plus **15**, mixed together as described previously. The agent (3) mentioned above may be diethylene glycol monoethyl ether, diethylene glycol monoethyl ether, or a combination of both for coupling the soap to water. This has a flash point of approximately 205 to 240 degrees F. and is a mutual solvent for all of the materials used in my process.

This preferred cleaning step comprises soaking the tested specimen for one to three minutes in a specially prepared bath utilizing approximately 1 pound of ingredients **13** plus **14** plus **15** as mixed together and previously described, plus 1 pound of either form of ingredient **15**, namely, the reaction product of triethanolamine with oleic or other of the fatty acids mentioned above, or potassium hydroxide reacted with oleic acid as mentioned in connection with ingredient **15**. To this mixture I add 18 grams of alkaline builder such as sodium pyrophosphate or sodium carbonate or trisodium phosphate and these materials are added to each gallon of water in the soaking bath preferably maintained at 160° to 180° F. for more rapid action. After the one to three minute soaking period, I prefer to rinse the specimen utilizing the previously described mixture of ingredients **13** plus **14** plus **15** at the rate of one part to 8000 to 12,000 parts of water which will then have a surface tension of about 34 dynes per sq. cm. so that the test piece can be dried without water spotting.

Preferably, for economic reasons, the specimen should be dry before cleaning, but my cleaning process will operate well in any case.

The advantage of using my invention over the previously used standard procedure of the Society of Automotive Engineers results in (1) better dispersion of the magnetic particles, (2) easier addition of the magnetic particle paste to the suspensoid oil, (3) elimination of clogging of equipment, (4) longer lasting suspension of the magnetic particles in the oil, (5) aids in the better wetting of the tested specimen as the test solution flows over it, and therefore an oil with greater viscosity and higher flash point can be used with no sacrifice in efficiency, (6) improves the travel of the magnetic particles to faults or cracks in the specimen, (7) improves the cleaning of the tested specimen by either a vapor degreaser or by water or by oil, (8) reduces the oxidation of the suspensoid oils during and after use, (9) reduces cleaning time for the specimen and eliminates approximately two-thirds of the cleaning of the testing machine, (10) inhibits rusting of the specimen, (11) produces a cleaner specimen part after the operation is completed, and (12) improves the action of a vapor-degreaser if such is used.

The following example illustrates the preparation of my additive for a suspensoid oil, the coating of iron oxide particles to form an iron oxide paste and the use of the additive and paste in preparing a test solution for detecting flaws in metal articles.

Example

A magnetic iron oxide paste component for a test solution for magnetic particle testing was prepared by adding and mixing 10 parts by weight of a dialkyl dimethyl ammonium chloride and one part by weight of a substituted oxazoline with an oxazole content of about 70 percent by weight with 85 parts by weight of "No. 7 Black Paste," a dispersion of 90 parts by weight of magnetic oxide of iron in 10 parts by weight of an oily medium which is a petroleum distillate of 46 degrees Baumé and 5 centistokes viscosity.

In the resultant oxide dispersion, the dialkyl dimethyl ammonium chloride (added as a de-flocculation agent for the iron oxide particles) was a liquid comprising a 75 percent by weight solution of the ammonium chloride in isopropanol. The two alkyl groups in the above dialkyl dimethyl ammonium chloride had the following approximate composition:

Alkyl Groups	No. of Carbon Atoms	Percent by Wt.
Octyl	8	8
Decyl	10	9
Dodecyl	12	47
Tetradecyl	14	18
Hexadecyl	16	8
Octadecyl	18	10

The substituted oxazoline, added to reduce interfacial tension of the film of oil around the iron oxide particle against water in the final mixture to be described later, was a nonvolatile cationic surface active agent having a specific gravity at (25/25° C.) of 0.92 to 0.93, a nitrogen content (Kjeldahl) of 3.8 to 4.1%, a color on the Gardner scale (1933) of 15 maximum, a viscosity of 25° C. of 122 centipoises, an oxazoline content of 70 percent and a molecular weight of approximately 350. A suitable oxazoline (2-methyl-4,4-dioctyl-2-oxazoline), having the above desired properties, may be prepared by reacting approximately equal moles of 2-amino-2-dioctyl-1-undecanol and acetic acid. The above ingredients, the quaternary ammonium salt, the substituted oxazoline, and magnetic particles were mixed by grinding in a ball mill for about 5 minutes at room temperature until the resultant treated particles could be dispersed quickly into either oil or water. This dispersing quality was checked by taking a small aliquot portion of the mixture and checking its dispersion at about 2 percent by weight in both oil and water solutions.

In mixing the quaternary ammonium salt, the substituted oxazoline, and the magnetic particles, other equipment and mixing times may be used to thoroughly disperse the same. By grinding the ingredients in a mill, usually only 3 or 4 minutes are necessary; by paddle mixing at high speeds, generally from about 8 to 48 hours are required.

An additive for the suspensoid oil was prepared by mixing 2 parts by weight of decyl benzyl sodium sulfonate, one part of a nonionic surfactant which is a reaction product of one mole of octyl phenol and three moles of ethylene oxide, and two parts by weight of an amine soap which is a reaction product of about equal moles of triethanol amine and lauric acid. After the three ingredients, corresponding to ingredients **13**, **14** and **15** in the flow sheet, were mixed, the mixture was heated with intermittent stirring to a temperature of 174° F. for 3 hours to cause a reaction between the three ingredients. The reaction batch was cooled. A precipitate formed and was allowed to settle and then filtered. The liquid filtrate was then used as a major portion of the additive for the suspensoid oil.

To complete preparation of an additive for the suspensoid oil, 58 parts by weight of the above described reaction product of **13**, **14** and **15** were mixed with 42 parts by weight of the same dialkyl dimethyl ammonium chloride described in preparing the magnetic oxide component. The above ingredients were mixed at 120° F., the liquid mixture becoming slightly turbid but quickly clearing with no other indication of a reaction evident.

A suspensoid oil (ingredient **17** on the flow sheet), the same oil used in the magnetic oxide paste, and having a 165° F. flash point (Tagliabue Open Cup), a viscosity

of 41 seconds and a Baumé of 46 degrees was used to suspend the oxide particles in the testing solution. Four parts by weight of the above described liquid mixture of ingredients **16** and the reaction product of **13**, **14** and **15** were added to 96 parts by weight of the suspensoid oil to provide a modified suspensoid oil component. Three parts by weight of oleic acid was added to the modified suspensoid oil to bring the pH down to about 6.5.

One part of the magnetic oxide paste component and 99 parts by weight of the modified suspensoid oil were thoroughly mixed to provide a test solution. The resultant test solution was used to check metal surfaces for flaws and cracks by the magnetic particle testing technique as set forth in the Report of the Iron and Steel Division of The Society of Automotive Engineers, adopted January 1941 and revised January 1942 in which the solution is poured over the test piece while the piece is subjected to a strong magnetic field. The test solution was excellent in all respects, the magnetic oxide particles remained deflocculated during the test and were removed easily from the test pieces and did not clog the machine.

Several test pieces were checked, one of which was cleaned in a vapor degreaser employing trichlorethylene. Another test piece was thoroughly and easily cleaned by soaking the piece in a bath of 1 part by weight of the reaction product of **13**, **14** and **15** and 1 part by weight of ingredient **15** (the reaction product of triethanol amine and lauric acid), 0.04 part by weight of sodium carbonate and 8.3 parts by weight of water. After soaking in the above bath, the test piece was rinsed in a bath of 1 part of the reaction product of **13**, **14** and **15** in 10,000 parts of water.

In the above example, good results can be obtained by using Arquad 2C, a dialkyl dimethyl ammonium chloride having alkyl groups of 8 to 18 carbon atoms, sold by Armour and Company, Chicago, Illinois, as the ingredients **12** and **16**. Likewise, the particular dialkyl dimethyl ammonium chloride used in the example can be substituted for in whole or part by other water insoluble dialkyl dimethyl ammonium chlorides having alkyl groups of about 8 to 18 carbon atoms such as octyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, octadecenyl, and iso octyl including 2-ethyl hexyl. Also, the substituents on the disubstituted dimethyl ammonium chlorides may also include in addition to alkyl groups, other aliphatic hydrocarbon groups such as alkenyl groups having about 8 to 18 carbon atoms and groups sometimes termed "coco" which are derived from coconut oil and also have 8 to 18 carbon atoms in their molecular chain.

Surprisingly, however, the above quaternary ammonium chloride is the only cationic wetting agent that can be used in the present invention, it having been found that other wetting agents including mono-alkyl trimethyl ammonium chlorides upset the delicate physical and chemical balance of the system and deflocculation of dispersed magnetic-oxide particles cannot be maintained. In addition dispersal of the magnetic oxide particles and their subsequent complete removal also cannot be accomplished.

In the above example and, in particular, the preparation of the reaction product of ingredients **13**, **14** and **15**; other alkyl phenol/alkylene oxide reaction products can be substituted in whole or part for the octyl phenol/ethylene oxide reaction product used. Suitable alkyl phenol/ethylene oxide reaction products are those prepared by reacting preferably about one equivalent weight of octyl phenol or other alkyl phenols having about 5 to 14 carbon atoms including pentyl phenol, hexyl phenol, 2-ethyl hexyl phenol, nonyl phenol, decyl phenyl and duodecyl phenol with about 2 to 12 equivalent weights of ethylene oxide. In some cases, while it is preferred that ethylene oxide be used, and be the major portion of the alkylene oxide component, part or even all of the ethylene oxide may be substituted for by propylene oxide; in a similar manner, at least a minor portion of the alkylene oxide may be propylene oxide-1,2; propylene oxide-1,3; or butylene-1,4-oxide.

Again referring to the reaction product of ingredients **13**, **14** and **15**, the reaction product (**15**) of triethanol amine and lauric acid may be substituted in whole or part by another water soluble amine soap such as the reaction product of (1) about one equivalent weight of a basic component such as an alkali metal hydroxide including sodium hydroxide, potassium hydroxide, ammonium hydroxide, an amine compound containing an oxygen atom as an ether atom or as an atom in a hydroxyl group such as triethanol amine, diethanol amine, monoethanol amine, and other amino hydroxy compounds having an amino group, a hydroxyl group, three to four carbon atoms and a molecular weight preferably between 89 and 106 including 2-amino-1-butanol; and 2-amino-2-methyl-1-propanol with (2) about .9 to 1.1 equivalent weights of an aliphatic hydrocarbon acid having about 3 to 18 carbon atoms such as saturated aliphatic acids including propionic, n-butyric, valeric, caproic, caprylic, capric, lauric, myristic and palmitic and unsaturated aliphatic hydrocarbon acids including undecylenic, linoleic, linolenic, and oleic. Surprisingly, stearic acid, a saturated aliphatic acid having 18 carbon atoms does not work while oleic acid with 18 carbon atoms does work. However, stearic acid reacts with an amine to form a water insoluble salt and is therefor unsuitable for use as an aliphatic acid for reaction with a base to prepare the necessary water soluble amine soap.

As previously indicated, ingredient **15** may also be di(2-ethyl hexyl) amine hydrochloride or other dialkyl amine hydrochloride having preferably alkyl groups of about 6 to 10 carbon atoms such as hexyl, octyl, nonyl and decyl.

Continuing to describe the reaction product of **13**, **14** and **15** and, in particular, the ingredient **13**, other alkyl aryl sodium sulfonates such as dodecyl benzyl sodium sulfonate, polypropyl benzene sodium sulfonate, octyl benzyl sodium sulfonate, tetradecyl benzyl sodium sulfonate, and octadecyl benzyl sodium salt are useful and are the preferred substitutes. Also suitable for use as ingredient **13** are alkali metal salts of sulphonic acids derived from petroleum sources and having an average molecular weight of generally about 250 to 750 and preferably about 400 to 520. In general, while the sodium salt is preferred, alkali metal soaps of potassium are of some use in the present invention.

The sulfonic acids used to form the alkali metal soap may be derived from either petroleum or alkyl aromatic acids. Suitable alkyl aryl sulphonic acids are polypropyl benzene sulfonic acid, didodecyl toluene sulfonic acid, octadecyl naphthalene sulfonic acid and octadecyl benzene sulfonic acid. As previously indicated the alkali metal soaps of these acids may have an average molecular weight of about 250 to 750.

The above described reaction product of ingredients **13**, **14**, and **15** is preferably prepared by reacting two parts of **13** to one part of **14** to two parts of **15**, although good results are obtained using equal amounts of all these ingredients. Also suitable are the ranges of 20 to 60 parts by weight of **13**, 10 to 50 parts by weight of **14**, and 20 to 60 parts by weight of **15**. Likewise, while the preferred temperature of the reaction is about 165 to 185 degrees, temperatures of 150 to 200 degrees may be used if the reaction is not prolonged at the higher temperatures, say for more than 2 hours and, also, if the time of reaction is extended to 5 to 8 hours at the low temperature. In any event, the resultant product has been found to be anionic in nature so that, surprisingly, even where it is mixed with a cationic wetting agent (**16**), it provides unusual results.

While it is not completely understood, the major portion and preferably about ⅔ of the reaction product is anionic while the balance, usually about ⅓ or in the range of ¼ to ⅔ of the product, is nonionic, apparently some

of the nonionic portion of the starting ingredients remaining unchanged.

While the reaction product of **13**, **14** and **15** was combined with ingredient **16** at 120 F. in the example, the same can be mixed effectively at a temperature preferably above normal room temperature, say 90° F. to a temperature of as high as 180° F. before a reaction occurs between the two components—one anionic and one cationic—and renders the mixture useless in the present invention.

Just after adding the above anionic-cationic mixture to the suspensoid oil, the pH of the former is lowered to about 5 to 7 and preferably 6.4 to 6.8 with a long chain aliphatic fatty acid having about 6 to 24 carbon atoms that is compatible with the hydrocarbon materials above described. While oleic acid is preferred to adjust the pH, other aliphatic acids such as hexyl, decyl, lauric, stearic and palmitic may be used. While acid materials such as hydrochloric acid, acetic acid etc. could drop the pH of the mixture, the resultant suspensoid oil would not keep the magnetic oxide particles deflocculated.

Further considering the mixture of the anionic reaction product of **13**, **14** and **15** and the cationic dialkyl dimethyl ammonium chloride (**16**), the preferred amounts of each ingredient are 57 to 59 parts by weight of the reaction product and 41 to 43 parts of the quaternary ammonium chloride although generally about 55 to 65 parts of the reaction product can be mixed with 35 to 45 parts of the chloride to provide a satisfactory modifying component for the suspensoid oil. When the above ranges ingredients are used, generally from about 1 to 10 parts of oleic acid are used to acidify 100 parts of the modifying additive mixture to balance the same.

In the above example, referring to the magnetic oxide paste component, other substituted oxazolines may be employed. Suitable substituted oxazolines are 2-methyl-4,4-dialkyl-2-oxazoline in which the alkyl radical has from about 1 to 10 carbon atoms such as methyl, ethyl, propyl, hexyl, octyl, nonyl and decyl although alkyl groups of 7 to 9 are highly preferred unless the methyl group on the 2 position is substituted for by a higher alkyl group, preferably ethyl or propyl so that the molecular weight of the oxazoline is preferably about 325 to 375.

Also referring to the oxide particle component, generally about 1 to 20 parts by weight of dialkyl dimethyl ammonium chloride are used per 80 to 99 parts by weight magnetic oxide particles. Likewise, about .1 to 3 parts by weight are used with the above amounts of oxide particles and chloride. In general then the above oxide particle mixture, moistened with about 3 to 20 parts by weight of oil, is used in an amount of generally 1/10 to 5 parts and, preferably ½ to 2 parts, by weight per 95 to 99 9/10 parts by weight of the modified suspensoid oil previously described.

In turn, as previously indicated, the modified suspensoid oil is made by using 90 to 99½ parts by weight of the oil and about ½ to 10 parts (and preferably 3 to 5 parts) by weight of the balanced wetting agent additive—namely the mixture of the liquid reaction product of **13**, **14** and **15** and the ingredient **16**.

What is claimed is:

A composition consisting essentially of (1) about 1/16 to 5 parts by weight of a mixture of (A) about 80 to 99 parts by weight of a mixture of about 90 parts by weight of fine magnetic iron oxide particles and 10 parts by weight of a light oil of about 46° Baumé having a Tagliabue Open Cup flash point of about 165° F. and a viscosity of about 41 seconds (Saybolt) and (B) about 1 to 20 parts by weight of a dialkyl dimethyl ammonium chloride in which the alkyl group has about 8 to 18 carbon atoms and (2) about 95 to 99 9/10 parts by weight of a modified suspensoid oil consisting essentially of about 90 to 99½ parts by weight of said light oil and about ½ to 10 parts by weight of an additive comprising (a) 55 to 65 parts by weight of a mixture obtained by heating at about 90° F. to 180° F., about 20 to 60 parts by weight of dodecyl benzene sodium sulfonate, about 10 to 50 parts by weight of a reaction product of lauric acid and triethanol amine and about 20 to 60 parts by weight of a reaction product of about one equivalent weight of an alkyl phenol in which the alkyl group has about 5 to 14 carbon atoms and about 2 to 12 equivalent weights of an alkylene oxide, and (b) about 35 to 45 parts by weight of a dialkyl dimethyl ammonium chloride in which the alkyl group has about 8 to 18 carbon atoms.

References Cited by the Examiner

UNITED STATES PATENTS

1,962,733	6/34	Davidson	252—62.5
2,106,882	2/38	Betz	252—62.5
2,365,253	12/44	De Forest	324—38
2,428,471	10/47	Pruitt	324—38
2,461,494	2/49	De Forest	324—38
2,478,951	8/49	Stakely	252—408
2,560,839	7/51	Ayo et al.	252—110
2,577,773	12/51	Lambert.	
2,663,809	12/53	Winslow	252—62.5 XR
2,675,356	4/54	Woodworth et al.	252—110
2,676,487	4/54	Clarke	252—408 XR
2,713,033	7/55	Cardwell et al.	252—148
2,723,239	11/55	Harvey	252—62.5
2,751,352	6/56	Bondi	252—62.5
2,754,266	7/56	Stegemeier et al.	252—9

FOREIGN PATENTS

642,820	6/62	Canada.

JULIUS GREENWALD, *Primary Examiner.*

LLOYD McCOLLUM, JAMES W. LAWRENCE, *Examiners.*