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STABLE METAL SOLS AND METHOD FOR PRODUCING THE SAME

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The present invention relates to stable colloidal dispersions (sols) of certain metals in liquid hydrocarbons and to an improved method of preparing such dispersions. More particularly it relates to stable colloidal dispersions in liquid hydrocarbon of metals characterized by negative standard oxidation-reduction (electrode) potentials at 25° C. in the electromotive force series of elements, and to an improved method of preparing these dispersions.

The standard oxidation-reduction potentials of the electromotive force series of elements are those tabulated, for instance, in Appendix II of "Reference Book of Inorganic Chemistry" by Latimer and Hildebrand (Macmillan Co., 1929), p. 367.

It is known in the art that the aforementioned metals characterized by negative potentials can be reduced to the form of colloidal dispersions (sols) by a variety of methods, the choice of which will depend on the metal involved. These methods include, for instance: chemical reduction of a solution of a metal salt, ultrasonic vibration of the metal, agitation of a liquid metal (e.g. mercury), application of Svedberg's high frequency arc, etc.

Likewise, it is known to produce colloidal dispersions of different so-called "noble" metals in one liquid as the dispersion medium (e.g. ethyl ether), and to transfer the dispersed metal into another dispersion medium (e.g. iso-octane, a lubricating oil, etc.) which is miscible with the first dispersion medium. For instance, after forming a very concentrated dispersion of a metal by centrifugation, the upper metal-free liquid can be decanted and the remaining sediment of the colloidal metal can be re-dispersed in another liquid, repeating the procedure several times, if necessary. Also, one can prepare a sol of a metal in a low-boiling liquid, such as ethyl ether, and add this sol to a higher-boiling liquid, e.g., a lubricating oil, and then remove the low-boiling liquid by distillation.

As a rule, colloidal dispersions (sols) of heavier "noble" metals are lyophobic and, consequently, relatively unstable, so that on standing these sols become rapidly precipitated. Peptizing agents or protective colloids, such as glue, gelatin, casein, gum arabic, etc., have been employed in aqueous systems to assist the process of dispersion of a solid by coating the dispersed particles thereof and preventing them from coalescence and eventual sedimentation. However, in the case of dispersions in liquid hydrocarbons of heavier metals, such as those of the gold and platinum series, stabilization with the aid of commonly known protective colloids is impractical, because generally such stabilizers are not soluble in liquid hydrocarbons. One might have expected that dispersant materials known to be soluble in hydrocarbons, such as various metal carboxylates, phenates, sulfonates, and the like, would exercise the desired stabilizing action, but it has been found that, even though the presence of these oil-soluble materials imparts a certain degree of stability to sols of metals in hydrocarbons, the effect is very slight and of a short duration. Coagulation of these sols proceeds relatively fast, and the metal settles out soon after the sol is left to stand or stored.

At the same time, it is realized that production of stable colloidal dispersions of heavier noble metals would open new avenues for the utilization of these metals in industrial practice, for instance, to reduce the surface-ignition tendencies of gasolines, to improve the lubricat-

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ing action of lubricating oils, to vary the dielectric properties of plastics, to impart new and attractive hues to materials and articles manufactured from plastics, etc.

I have found that lasting colloidal dispersions or sols of metals characterized by negative electrode potentials at 25° C., using liquid hydrocarbons as the dispersion media, can be produced by dispersing the metal in a liquid hydrocarbon in the presence of a small but stabilizing amount of an oil-soluble macromolecular dispersant material produced by copolymerizing monomeric materials, such as are defined in the following description.

At this point certain definitions are in order:

The term "colloidal dispersions" or "sols," as employed herein, refers to dispersions of solid materials, such as metals usually having particle sizes in the range from 1 to 100 mμ i.e., 10 to 1000 angstroms.

The term "heavier noble metals" as employed in this specification shall refer to those metals characterized by negative standard oxidation-reduction (electrode) potentials at 25° C. as defined, for instance, by Latimer and Hildebrand in their "Reference Book of Inorganic Chemistry," 1929 edition, at p. 367, or in "Handbook of Chemistry and Physics," edited by C. D. Hodgman, 37th edition (Chemical Rubber Publishing Co.) at p. 1660. The negative oxidation-reduction (electrode) potentials there defined are referred to the potential zero of the hydrogen-hydrogen ion couple.

The term "oil-soluble" as used in this specification hereinafter is intended to mean soluble in liquid hydrocarbons.

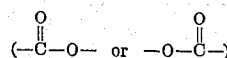
The group of polymeric macromolecular materials effective in stabilizing, that is, in preventing or at least significantly retarding the coalescence of the colloidal size particles of metal in the dispersion and the eventual precipitation (sedimentation) of the solid metal phase from the liquid hydrocarbon phase (dispersion medium), comprises any material of the known class of oil-soluble polymeric stabilizers for colloidal dispersions. For present purposes, a preferred group consists of copolymers of (A) at least one oil-solubilizing monomer having a single ethylenic linkage and containing a monovalent hydrocarbon group of from 8 to 30 aliphatic carbon atoms and (B) at least one polar monomer selected from the group consisting of unsaturated aliphatic mono- and dicarboxylic acids of 3 to 6 carbon atoms, polyalkylene glycol esters of these acids and alkyl ethers thereof, amino-alkyl esters of the aforesaid acids in which the amino-alkyl group contains not more than 8 carbon atoms, and finally, N-vinyl pyrrolidones.

The oil-solubilizing monomer portion (A) of the macromolecular polymeric materials effective as stabilizers for colloidal dispersions (sols) of metals in accordance with the invention can be any compound having at least one ethylenic (>C=C<) linkage, at least one monovalent hydrocarbon substituent of from 8 to 30 aliphatic carbon atoms, and polymerizing through its ethylenic linkage with the monomer portion (B) containing a polar group.

The oil-solubilizing monomers (A) may be represented by the general formula $R_1(G^1)_nCH=CH(G)_nR_2$, in which R_1 and R_2 are members of the group consisting of hydrogen and hydrocarbon radicals of from 8 to 30 carbon atoms; at least one of radicals R_1 and R_2 containing an aliphatic group of from 8 to 30 carbon atoms; G and G^1 are members of the class consisting of oxy (-O-), carbonyl



and carbonyloxy



groups and combinations thereof with not more than two alkylene groups of from 1 to 7 carbon atoms each; and n and n' are 0 or 1.

Preferably, the oil-solubilizing monomers (A) are higher C_8 - C_{30} alkyl esters of α,β -unsaturated C_3 - C_6 aliphatic mono- and dicarboxylic acids. The alkyl portions of these esters may contain from 8 to 30, and preferably from 10 to 20 carbon atoms, while the C_3 - C_6 aliphatic carboxylic acids which may be employed to prepare these alkyl esters may be selected among acids, such as acrylic, methacrylic, crotonic, tiglic, angelic, α -ethylacrylic, maleic, α -methylcrotonic, α -ethylcrotonic, β -ethylcrotonic, fumaric, and the like.

The unsaturated aliphatic monocarboxylic acids in the group of monomers (B) may be any of the C_3 - C_6 aliphatic mono- and dicarboxylic acids, e.g., acrylic, methacrylic, tiglic, maleic, itaconic, mesaconic, and the like. The more preferred acids are acrylic and methacrylic.

The polyalkylene glycols and alkyl ethers thereof employed to form the corresponding esters of unsaturated C_3 - C_6 aliphatic mono- and dicarboxylic acids, as suitable monomers of the group (B) for the preparation of the macromolecular copolymer materials, range in molecular weight from about 150 to about 30,000 and preferably from about 200 to 10,000. Polyethylene glycols and their alkyl ethers are preferred. Those of molecular weight in the range from about 400 to about 2,000 are particularly suitable. All of these polyalkylene glycol materials are readily obtainable in accordance with the procedures known in the art.

As indicated hereinbefore, the group of monomers (B) also includes two kinds of nitrogen-containing materials, namely, N-vinyl pyrrolidones and aminoalkyl esters of unsaturated C_3 - C_6 aliphatic mono- and dicarboxylic acids. In these latter, the aminoalkyl group $-\text{NR}'\text{R}''$ may contain straight-chain or branched-chain alkyl groups, or one alkyl chain and a hydrogen, attached to the nitrogen atom. Suitable N-vinyl pyrrolidones are, for instance, 3-methyl-1-vinyl pyrrolidone, 2-methyl-1-vinyl pyrrolidone, 3-propyl-1-vinyl pyrrolidone, 4-propyl-1-vinyl pyrrolidone, 2-ethyl-1-vinyl pyrrolidone, 3-ethyl-1-vinyl pyrrolidone, 4-ethyl-1-vinyl pyrrolidone, 2-butyl-1-vinyl pyrrolidone, 2,3,4-trimethyl-1-vinyl pyrrolidone, 2,2-dimethyl-1-vinyl pyrrolidone, 3,3-dimethyl-1-vinyl pyrrolidone, 4,4-dimethyl-1-vinyl pyrrolidone, 2-ethyl-3-methyl-1-vinyl pyrrolidone, 3-ethyl-2-methyl-1-vinyl pyrrolidone, and other lower C_1 - C_4 alkyl-substituted derivatives of N-vinyl pyrrolidone which is obtained in a known manner by reacting acetylene with α -pyrrolidone in the presence of a strongly basic catalyst, such as potassium hydroxide.

When the aforescribed macromolecular materials are present in the colloidal dispersions in liquid hydrocarbons of heavier metals, i.e., ones characterized by negative oxidation-reduction potentials of 25°C . in the amounts ranging from about 25 to about 200%, based on the weight of the colloidal metal in the dispersion, lasting stable metal dispersions are secured. These dispersions contain up to 2% by weight of the metal. In many cases, even larger quantities of heavier noble metals can be thus colloiddally dispersed in liquid hydrocarbons, and the resulting sols remain stable for days, weeks and even months at a time.

The macromolecular copolymer materials suitable as stabilizers for metal sols, according to the invention, have apparent molecular weights in the range from about 2,000 to as high as 1,000,000, as determined by the standard light-scattering methods (e.g., one described by D'Alelio in "Fundamental Principles of Polymerization," Wiley and Sons, 1952, pp. 256-267). For practical purposes, molecular weights of from 100,000 to 1,000,000 are most suitable.

Particularly effective as stabilizers for the purposes of the present invention are those macromolecular copolymers in which the ratio of the weight of bound oxygen

to the weight of the macromolecule lies between 0.3 and 1.6%.

The preparation of the oil-soluble copolymers operative as stabilizers for the dispersions of heavier metals in liquid hydrocarbons in accordance with the invention, starting from monomers of the types (A) and (B) described hereinabove, is entirely straightforward and follows the conventional procedures of the art, such as bulk, solution or emulsion polymerization with the aid of suitable polymerization initiators or catalysts. Preferably the polymerization is effected in an inert organic medium (solvent), such as benzene, in the presence of a free-radical type initiator, (in amounts which may range from 0.1 to 10% by weight), for instance, benzoyl peroxide, α,α' -azodiisobutyronitrile, at temperatures which may range from 300°F . to 350°F .

One embodiment of such polymerization is illustrated below by an example in which dodecyl methacrylate as monomer (A) and dodecyl ether-capped polyethylene glycol (mol wt. 1600 average) methacrylate as monomer (B) were employed to prepare the macromolecular copolymer suitable as a stabilizer for metal sols in accordance with the invention.

Into a 500 cc. three-necked flask, equipped with a mechanical stirrer, a reflux condenser, and a burette, there was charged 106 g. of dodecyl methacrylate (0.418 mol), 14 g. of dodecyl ether-capped polyethylene glycol methacrylate (0.0075 mol), and 213 g. of benzene, together with 0.01% by weight of α,α' -azodiisobutyronitrile as a catalyst. The polymerization was carried out at reflux, after sweeping out the whole system with nitrogen. The reaction temperature was held at 190°F . and the catalyst was added in increments every 15 minutes to maintain a constant catalyst level. After $7\frac{1}{2}$ hours the conversion was equal to 86%. The product had an alkyl to dodecyl ether-capped polyethylene glycol methacrylate ratio of 88 to 1. The average molecular weight of the product was approximately 280,000.

The metals which can be reduced into stable colloidal dispersions or sols in liquid hydrocarbons in accordance with the invention by employing the oil-soluble macromolecular materials described hereinabove are those of the gold series (Group 1B of the Periodic System), namely, gold, silver, and copper; those of the palladium-platinum series (Group 8 of the Periodic System), namely, platinum, palladium, ruthenium, rhodium, osmium and iridium; as well as mercury, antimony, bismuth and arsenic. In other words, the metals which can be thus dispersed in liquid hydrocarbons to form stable sols therewith are metals characterized by negative standard oxidation-reduction potentials at 25°C . in the previously mentioned electromotive-force series of elements, in which series hydrogen has an electrode potential of 0 at 25°C .

Any liquid hydrocarbon can be employed as the dispersion medium or solvent. Typical solvents are benzene, n-pentane, hexane, cyclohexane, iso-octane, as well as mixtures of hydrocarbons, such as gasoline, white oil, lubricating oil, kerosene, fuel oil, etc.

The macromolecular copolymer materials which impart stability to the dispersions of the heavier metals in hydrocarbon media in accordance with the invention are employed in amounts which range from about 0.02 to about 10.0% by weight, based on the hydrocarbon solvent serving as the dispersion medium for the metal.

The following examples serve to illustrate the preparation of dispersions (sols) of different heavier metals characterized by negative electrode potentials in accordance with the invention.

EXAMPLE I.—PREPARATION OF GOLD SOLS

0.5 g. of gold chloride ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was dissolved in 5 ml. of ethyl ether, and the solution transferred to one-liter graduate, rinsing the weighing bottle with an additional 5 ml. of ether. 200 ml. of a 20% weight solution of Aerosol OT (dioctylsulfosuccinate) in iso-octane was

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added to the resulting ether solution. The mixture was shaken until the solution became clear, whereupon the graduate was filled to one-liter mark with iso-octane. The gold sol was produced by reduction of this iso-octane solution with 120 ml. of saturated (0.05 N) ether solution of 95% hydrazine. This latter solution was obtained by swirling together hydrazine and ether and decanting the ether layer. Reduction of gold was complete in about one hour. The reduced mixture was allowed to stand 24 hours, whereupon the dispersion was purified by centrifuging at $30,000\times$ gravity for 30 minutes and decanting 90% of the supernatant liquid. The remaining 10% bottoms was diluted with iso-octane to the original volume and re-centrifuged. After decanting again 90% of the supernatant liquid, the remainder was combined with 0.2 weight percent solution of the desired macromolecular stabilizer of the present invention, e.g., a quadripolymer of "Oxo"-tridecyl methacrylate, n-dodecyl methacrylate, octadecyl (tallow) methacrylate and polyethylene glycol (1625 mol wt.) monododecyl ether methacrylate.

The "Oxo"-tridecyl methacrylate was derived from "Oxo"-tridecyl alcohol produced by the "Oxo" process from tri-isobutylene. Octadecyl methacrylate was derived from tallow.

Gold dispersions obtained in this manner remained stable for 48 hours, and for a long time thereafter (weeks and even months) showed no impairment of stability.

EXAMPLE II.—PREPARATION OF PLATINUM SOLS

0.84 g. of chloroplatinic acid (H_2PtCl_6) was dissolved in 42 ml. of distilled water. 10 ml. of the resulting solution was added to 400 ml. of a 5% solution of Aerosol OT in iso-octane. Platinum was reduced by employing sufficient hydrazine in the same manner as described in Example I for gold dispersions. The reduction was complete in about 2 hours. After this, 90% of the water and hydrazine was stripped off in a still, and the remaining solution was centrifuged at $30,000\times$ gravity. 75% of the metal-free top portion of the centrifuged liquid was decanted, and 42 ml. of the platinum-containing bottoms was combined with iso-octane which contained 0.5% by weight of a macromolecular stabilizer, such as a copolymer C_{12} - C_{18} methacrylate and diethyl aminoethyl methacrylate. The mixture was centrifuged at $30,000\times$ gravity for one hour and decanted again, leaving 50 ml. of bottoms which was diluted with the iso-octane solution of the macromolecular stabilizer to 565 ml. This procedure, centrifuging, decanting and diluting, was repeated once more.

The finally obtained platinum sols were found to be stable after 48 hours, and remained stable for a long time thereafter (at least several weeks).

EXAMPLE III.—PREPARATION OF SILVER SOLS

Silver sols ranging in color from yellow to green were prepared by treating ammoniacal silver oxide with a solution of Aerosol OT in iso-octane, using procedures similar to those described in Example II, and adding to the mixture a 1% solution of a macromolecular stabilizer in iso-octane, viz., copolymer of alkyl methacrylate and diethyl aminoethyl methacrylate. Thereafter silver was reduced with hydrazine in ethereal benzene solution. The same purification sequence of centrifugation, decantation and dilution steps, as described in Example II for platinum sols, was followed. These silver sols again remained stable for 48 hours and a long time thereafter.

EXAMPLE IV.—PREPARATION OF COPPER SOLS

Ammoniacal solution of cupric oxide was combined with a solution of Aerosol OT in iso-octane, and to the resulting mixture there was added a 1% solution in iso-octane of the same macromolecular stabilizer as in Example III. Thereupon, copper was reduced with hydrazine in the same manner as shown in the preceding examples, and the same sequence of centrifugation, decantation and

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dilution was followed to obtain stable sols of pure copper.

In contrast to the stable metal dispersions produced with the aid of the particular effective macromolecular stabilizers of the invention, as illustrated by the above examples, a number of the known oil-soluble dispersants, such as metal phenates, carboxylates and sulfonates, failed to provide the desired lasting stability to the sols of heavier noble metals in liquid hydrocarbons.

The stability of the dispersions (sols) being a function of the particle-size of the dispersed material (in the present case, of the metal), upon prolonged standing the particles tend to agglomerate and grow in size forming small clumps until finally settling out (sedimentation) takes place. Polar compounds tend to coagulate metal sols. Bivalent ions are more effective than monovalent ions, and trivalent ions are even more so effective, in causing precipitation of the metal from its dispersion in a liquid hydrocarbon. Therefore, addition of polar compounds provides a measure of the relative stability of different sols containing different dispersants, and permits selection of a most suitable macromolecular stabilizer for each particular metal-in-hydrocarbon dispersion to be prepared in accordance with the invention.

Among the several series of sols of different metals, a representative series of gold sols has been selected to illustrate the superior stability of the metal sols prepared in accordance with the invention. Gold sols with smallest (colloidal size) particles are deep red in color. As the particles of gold agglomerate and form larger clusters, they change in color from red to violet, then to purple, and, finally, to blue.

In the particular test series, 5 ml. of concentrated gold sol, prepared as described in Example I, was mixed with 45 ml. of a 1% solution of the macromolecular stabilizer. The appearance of the sol was noted immediately following its formation and also after standing for 48 hours.

Table I.—Effect of various oil-soluble dispersant materials on stability of gold sols

Additive	Initial color of sols	Color of sols after 48 hours
Pentaerythritol mono-oleate	Red	Blue, coagulated.
Calcium polypropylene phenate, sulfurized (4.5% Ca)	do	Do.
Copolymer of dodecyl methacrylate, methacrylic acid and decaethylene glycol octadecyl ether methacrylate (mol ratio 7.3/0.8/0.2)	do	Red.
Copolymer of "Oxo"-tridecyl methacrylate octadecyl methacrylate and decaethylene glycol tridecyl ether methacrylate (mol ratio 10.2/6.8/1.0)	do	Do.
Copolymer of dodecyl methacrylate and diethyl aminoethyl methacrylate	do	Do.
Copolymer of dodecyl methacrylate and N-vinyl pyrrolidone (mol. wt. 350,000)	do	Do.
Copolymer of dodecyl methacrylate and N-vinyl pyrrolidone (mol. wt. 550,000)	do	Do.
Copolymer of dodecyl methacrylate and methacrylic acid.	do	Do.

The results in this table show that the oil-soluble metal salts, e.g., phenates, carboxylates, sulfonates, etc., and other low molecular weight materials, e.g., organic esters, although known to be effective as dispersants, do not provide stable metal sols. On the other hand, the oil-soluble macromolecular copolymer stabilizers, described hereinbefore as being effective according to the invention, in all instances assure stability to metal sols which persist for 48 hours and longer.

Furthermore, the macromolecular stabilizers of this invention often act to protect the metal dispersion from the adverse (destabilizing) effect of polar compounds. This is shown by the data in Table II relative to the appearance of representative gold dispersions containing different stabilizers after the addition thereto of several polar compounds: diethyl amine, quinoline, acetic acid, and water.

Table II.—Effect of different polar compounds on stability of gold sols

APPEARANCE OF SOLS AFTER ADDITION OF POLAR COMPOUNDS
[Initial color of all sols on their formation—Red]

	Oil soluble-dispersant				
	Pentaerythritol mono-oleate	Sulfurized calcium polypropylene phenate (4.5% Ca)	Copolymer of mixed (C ₄ -C ₁₈) alkyl methacrylates	Calcium petroleum (lubr. oil) sulfonate	Copolymer of dodecyl methacrylate, methacrylic acid and decaethylene glycol octadecyl methacrylate
Polar compound: 2 ml. diethylamine.....	Coagulated.....	Coagulated.....	Coagulated.....	Coagulated.....	Red.
1 ml. iso-octane solution of quinoline (saturated).	do.....	do.....	Blue coagulated.....	do.....	Red-violet.
1 ml. acetic acid.....	do.....	do.....	Coagulated.....	Coagulated.....	Purple.
1 ml. water.....	do.....	do.....	do.....	do.....	Partly coagulated.

	Oil-soluble dispersant		
	Copolymer of "oxo"-tridecyl methacrylate, dodecyl methacrylate, octadecyl methacrylate, and polyethylene glycol (mol wt. 1625) monodecyl ether methacrylate	Copolymer of "oxo"-tridecyl methacrylate, octadecyl methacrylate, and decaethylene glycol tridecyl ether methacrylate	Copolymer of dodecyl methacrylate and diethyl amino-ethyl methacrylate
Polar compound: 2 ml. diethylamine.....	Red.....	Red.....	Coagulated.
1 ml. iso-octane solution of quinoline (saturated).	do.....	do.....	Violet-blue, partly coagulated.
1 ml. acetic acid.....	do.....	do.....	Red-violet.
1 ml. water.....	Red.....	do.....	do.....

	Oil-soluble dispersant		
	Copolymer of dodecyl methacrylate and N-vinyl pyrrolidone (mol wt. about 350,000)	Copolymer of dodecyl methacrylate and N-vinyl pyrrolidone (mol wt. about 550,000)	Copolymer of dodecyl methacrylate and methacrylic acid
Polar compound: 2 ml. diethylamine.....	Red.....	Red.....	
1 ml. iso-octane solution of quinoline (saturated).	Violet.....	do.....	
1 ml. acetic acid.....	Red-violet.....	Red-violet.....	Bluish-red.
1 ml. water.....	do.....	do.....	Red.

It is clearly seen from the data in Table II that carboxylates, phenates and other known oil-soluble dispersants fail to prevent coagulation after the addition of the polar compounds to the dispersions. On the other hand, the macromolecular copolymer materials, described as the effective stabilizers for metal sols in accordance with the invention, generally provide sufficient protection against coagulation due to the addition of polar compounds. Because admixture of traces of the polar compounds into the sols is apt to occur on their standing and in storage, this property of the macromolecular stabilizers is particularly important.

The exact mechanism of stabilization of metal sols is not fully understood. However, it is surmised that the macromolecules of the stabilizer with polar groups scattered along its main chain wrap themselves around the colloidal particles of metal, forming an envelope which is rendered tight by the adherence of the polar groups in the structure of these molecules to the metal particle. Thus, the tendency of the metal particles to agglomerate (aggregate) is reduced, and the traces of polar compounds which happen to come into contact with the dispersions are less likely to displace the envelope formed by the macromolecular stabilizer, or to pass through this envelope, and thus to cause coagulation.

At this point, it may be noted that dispersion of metals in certain hydrocarbons, such as benzene or isooctane, prepared by using the high-frequency electric arc, may contain relatively large amounts of finely dispersed carbon together with the colloidal metal. When this represents

a problem, it will be preferred to form the sols in ethyl ether, n-pentane or the like materials miscible with hydrocarbons, and from these solutions one can then readily transfer the colloidal-dispersed metal into the desired hydrocarbon solvent or medium by the procedures described earlier in this specification.

As pointed out hereinbefore, the operative concentration of the macromolecular stabilizer may vary from about 25 to about 200 percent by weight, based on the metal in the dispersion, depending on the particular copolymer employed as the stabilizer, the metal to be dispersed, the hydrocarbon medium employed and the degree of stability desired. A concentration of at least 0.02 percent by weight based on the hydrocarbon medium will be used, without exceeding under normal conditions the concentration of about 10.0 percent by weight, based on the hydrocarbon solvent.

The resulting stable dispersions of heavier metals may be thereafter added to different hydrocarbon fuels and oils for the purpose of improving their properties. It is expected that the addition of the stabilized metal sols of this invention to gasoline should reduce the surface-ignition and the valve-burning in internal combustion engines and should improve thereby the overall engine performance. Likewise, incorporation of these metal sols into plastics, prior to the molding and shaping of these latter to their permanent form, serves to achieve a variety of very attractive hues for the finished plastic articles.

Since many widely different embodiments of the present

invention are contemplated to be feasible without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited to the specific examples offered merely for the sake of illustration, except as defined in the following claims.

This application is a continuation-in-part of my application Serial No. 815,249, filed by me on May 25, 1959, in the U.S. Patent Office, and presently abandoned.

I claim:

1. As a new composition, a stable colloidal dispersion in a liquid hydrocarbon of a metal characterized by a negative standard oxidation-reduction potential at 25° C. in particles ranging in size from 10 to 1,000 angstroms, said dispersion comprising: a liquid hydrocarbon; up to 2% by weight of the metal dispersed therein, based on the finished dispersion; and a small amount from about 0.02 to about 10.0% by weight, based on said liquid hydrocarbon, of an oil-soluble macromolecular copolymer of (A) at least one oil-solubilizing monomer having a single polymerizable ethylenic linkage and a monovalent hydrocarbon group of from 8 to 30 aliphatic carbon atoms, and (B) at least one polar monomer selected from the group consisting of unsaturated C₃-C₆ aliphatic mono- and dicarboxylic acids, polyethylene glycol esters of said acids and alkyl ethers thereof, aminoalkyl esters of said acids wherein the aminoalkyl group consists of not more than 8 carbon atoms, and N-vinylpyrrolidones, the apparent molecular weight of said copolymer lying in the range from about 2,000 to 1,000,000.

2. As a new composition, a stable colloidal dispersion in a liquid hydrocarbon of a metal characterized by a negative standard oxidation-reduction potential at 25° C. in particles ranging in size from 10 to 1,000 angstroms, said dispersion comprising: a liquid hydrocarbon; up to 2% by weight of the metal dispersed therein, based on the dispersion; and from about 0.02 to about 10.0%, based on said liquid hydrocarbon of an oil-soluble macromolecular copolymer of (A) at least one oil solubilizing monomer having a single polymerizable ethylenic linkage and a monovalent hydrocarbon group of from 8 to 30 aliphatic carbon atoms, and (B) at least one polar monomer selected from the group consisting of unsaturated C₃-C₆ aliphatic monocarboxylic acids, polyethylene glycol esters of said acids and alkyl ethers thereof, aminoalkyl esters of said acids wherein the amino alkyl group consists of not more than 8 carbon atoms, and N-vinyl pyrrolidones, the apparent molecular weight of said copolymer lying in the range of from about 100,000 to 1,000,000.

3. As a new composition, a stable colloidal dispersion in a liquid hydrocarbon of a metal characterized by a negative oxidation-reduction potential at 25° C. in particles ranging in size from 1 to 1,000 angstroms, said dispersion comprising: a liquid hydrocarbon; up to 2% by weight of the metal dispersed therein, based on the finished dispersion; and from about 0.02 to about 10.0% by weight, based on said liquid hydrocarbon, of an oil-soluble macromolecular copolymer of (A) at least one oil-solubilizing monomer having a single polymerizable ethylenic linkage and a monovalent hydrocarbon group of from 8 to 30 aliphatic carbon atoms and (B) at least one polar monomer selected from the group consisting of unsaturated C₃-C₆ aliphatic monocarboxylic acids, polyethylene glycol esters of said acids and alkyl ethers thereof, aminoalkyl esters of said acids wherein the aminoalkyl group consists of not more than 8 carbon atoms, and N-vinyl pyrrolidones, the ratio of the weight of the bound oxygen in said macromolecular copolymer to the weight of the macromolecule being in the

range of from about 0.3 to about 1.6%, and the apparent molecular weight of said copolymer lying in the range of about 2,000 to 1,000,000.

4. As a new composition, a stable colloidal dispersion in a liquid hydrocarbon of a metal characterized by a negative standard oxidation-reduction potential at 25° C. in particles ranging in size from 10 to 1,000 angstroms, said dispersion comprising: a liquid hydrocarbon; up to 2% by weight of the metal dispersed therein, based on the finished dispersion; and a small amount from about 0.02 to about 10.0% by weight, based on said liquid hydrocarbon, of an oil-soluble macromolecular copolymer of (A) at least one C₃-C₃₀ alkyl ester of an unsaturated C₃-C₆ aliphatic monocarboxylic acid and (B) at least one polar monomer selected from the group consisting of unsaturated C₃-C₆ aliphatic mono- and dicarboxylic acids, polyethylene glycol esters of said acids and alkyl ethers thereof, aminoalkyl esters of said acids wherein the amino-alkyl group consists of not more than 8 carbon atoms, and N-vinyl pyrrolidones, the apparent molecular weight of said copolymer lying in the range from about 2,000 to 1,000,000.

5. As a new composition, a stable colloidal dispersion in a liquid hydrocarbon of a metal characterized by a negative standard oxidation-reduction potential at 25° C. in particles ranging in size from 10 to 1,000 angstroms, said dispersion comprising: a liquid hydrocarbon; up to 2% by weight of the metal dispersed therein, based on the finished dispersion; and a small amount from about 0.02 to about 10.0% by weight, based on said liquid hydrocarbon, of an oil-soluble macromolecular copolymer (A) an C₃-C₃₀ alkyl methacrylate and (B) at least one polar monomer selected from the group consisting of unsaturated C₃-C₆ aliphatic mono- and dicarboxylic acids, polyethylene glycol esters of said acids and alkyl ethers thereof, aminoalkyl esters of said acids wherein the aminoalkyl group consists of not more than 8 carbon atoms, and N-vinyl pyrrolidones, the apparent molecular weight of said copolymer lying in the range from about 2,000 to 1,000,000.

6. In the preparation of a stable colloidal dispersion in a liquid hydrocarbon of a metal characterized by a negative standard oxidation-reduction potential of 25° C. in particles ranging in size from 10 to 1,000 angstroms, the improved method of dispersing up to 2% by weight of the metal, based on the finished dispersion, in the liquid hydrocarbon in the presence of from about 0.02 to about 10.0% by weight, based on said liquid hydrocarbon, of an oil-soluble macromolecular copolymer of (A) at least one oil-solubilizing monomer having a single polymerizable ethylenic linkage and a monovalent hydrocarbon group of from 8 to 30 aliphatic carbon atoms and (B) at least one polar monomer selected from the group consisting of unsaturated C₃-C₆ aliphatic mono- and dicarboxylic acids, polyethylene glycol esters of said acids and alkyl ethers thereof, aminoalkyl esters of said acids wherein the aminoalkyl group contains not more than 8 carbon atoms, and N-vinyl pyrrolidones, the apparent molecular weight of said copolymer lying in the range from about 2,000 to 1,000,000.

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JULIUS GREENWALD, *Primary Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,180,835

April 27, 1965

John B. Peri

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 14, for "hydrocarbon" read -- hydrocarbons --; column 6, line 8, for "meals" read -- metals --; column 9, line 37, after "the" insert -- finished --; line 54, for "1" read -- 10 --; line 70, for "macromolecule" read -- macromolecule --.

Signed and sealed this 28th day of September 1965.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents