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# COLLOIDAL METAL IN NON-AQUEOUS MEDIA

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## ABSTRACT OF THE DISCLOSURE

Colloidal metal having an average diameter range from about 45 A. to about 300 A. in a non-aqueous medium is prepared by reduction of a water soluble metal salt by a reducing agent, such as, a borohydride, in the presence of a fatty acid or fatty acid salt, such as, myristic acid or myristate, in an aqueous solution. Noble metals are preferred, particularly silver and palladium. An organic water immiscible solvent, such as, toluene, is added to the solution and acidified. The organic solvent phase is separated with the colloidal metal suspended therein.

## BACKGROUND OF THE INVENTION

The invention concerns a form of stable colloidal metal having an average diameter size range of from about 47 A. to about 300 A. in a non-aqueous medium, and the method of making.

Colloidal metal, such as, silver, has been prepared for many purposes by the reduction in aqueous solutions of a metal salt, such as, silver nitrate. For example, silver salt reducing agents; such as, p-phenylenediamine and hydroquinone, will readily reduce silver nitrate in aqueous solution to produce a yellow colloidal dispersion of silver. Dispersions of this type have been suggested for use in photographic materials, for example, integral filter layers in light-sensitive multilayer photographic color films for purpose of shielding certain emulsion layers from blue light.

A typical yellow colloidal dispersion known as Carey Lea Silver is a product of the alkaline dextrin reduction of silver nitrate. Colloidal silver has also been prepared by the reduction of silver nitrate by potassium borohydride in the presence of gelatin as a peptizing agent. However, it has been desirable to have colloidal metal; such as, colloidal silver, in a non-aqueous solvent; such as, one of those employed in a dry physical development system. The colloidal silver dispersion; such as, Carey Lea Silver, prepared by known methods, coagulates when added to a non-aqueous solvent; such as, toluene.

It has been desirable to prepare a stable, coloidal system in non-aqueous media of colloidal silver or similar metal and to have this dispersion free of reducing agents, salt, and by-products of metal reduction since the residual chemicals often are photographically active.

One object of this invention is to provide stable, non-aqueous dispersions of colloidal metals. It is another object to provide a method for preparation of stable and non-aqueous dispersions of colloidal metals.

## SUMMARY OF THE INVENTION

Stable colloidal metals and dispersions in a non-aqueous medium are obtained by reducing a water soluble metal salt of a metal with a reducing agent in the presence of a fatty acid having 10 to 22 carbon atoms in an aqueous solution, adding about 100 to 150 percent by volume of an organic solvent, which is substantially immiscible with water and acidifying the solution to extract the colloidal metal into the organic solvent phase.

In a preferred embodiment, stable colloidal silver dispersions are obtained by a reduction of aqueous silver



nitrate by potassium borohydride in the presence of sodium myristate. When the resulting product is acidified in the presence of about an equal volume of toluene, colloidal silver and myristic acid are extracted into the toluene phase.

## DESCRIPTION OF THE PREFERRED EMBODIMENT

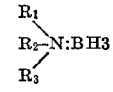
An aqueous solution of a water soluble metal salt, preferably a noble metal salt of a metal, such as, silver, palladium, platinum, gold, mercury, rhodium, ruthenium and osmium, is prepared.

The concentration of the metal salt in the aqueous solution can be varied widely, but in a convenient method, sufficient salt is added to provide about 0.05 to about 0.2 molar solution of the salt.

To this solution is added a fatty acid or fatty-acid salt, having 10 to 22 carbon atoms. In the event that the fatty acid is not water soluble, a water-soluble salt is used, preferably an alkali metal salt; such as, potassium, sodium, or the like. The amount of the fatty acid or fatty-acid salt may be varied widely but is preferably about an equal molar amount to the metal salt. Any suitable fatty acid having from 10 to 22 carbon atoms may be used; including, capric, lauric, myristic, palmitic, stearic, arachidic, behenic, etc. Although saturated fatty acids are preferred, it will be appreciated that unsaturated acids having 10 to 22 carbon atoms may also be used. An alkaline pH is maintained.

A silver salt is formed with the fatty acid in the aqueous solution and to this is added a reducing agent. Various reducing agents may be used, including those which are known in the prior art, particularly for reducing silver nitrate to colloidal silver which reduce at alkaline pH and are water soluble. However, a reducing agent having a standard potential more negative than −0.30, e.g., a borohydride or hypophosphite, is preferred. Particularly useful reducing agents which can be used include borohydrides, such as alkali (e.g., sodium, potassium, ammonium, etc.) borohydrides, which have a standard potential of −1.24 measured at 25° C. and hypophosphites ($H_2PO_2^{\ominus}$); such as, hypophosphorous acid ($H_3PO_2$), which has a standard potential ($E^o$) of −0.50 measured at 25° C. See W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solution", 2nd Edition, Prentice Hall, Inc., New York, 1952. The $E^o$ values are in keeping with the IUPAC convention as to sign. Preferred borohydrides for use in this invention are the alkali metal borohydrides and more particularly sodium or potassium borohydride.

Water-soluble amine-boranes having the following structure are also useful reducing agents:



wherein, within the limitation that the amine-borane is stable in aqueous solution, the groups $R_1$ and $R_2$ separately represent hydrogen atoms or alkyl, aryl or aralkyl groups and $R_3$ represents an alkyl, cycloalkyl, aryl or aralkyl group or $R_1$ and $R_2$ constitute with the nitrogen atom a heterocycle and $R_3$ is then a hydrogen atom.

Referring to the foregoing formula, examples of alkyl groups are methyl, ethyl, propyl and isopropyl, an example of cycloalkyl is cyclohexyl, examples of aryl are phenyl and naphthyl which can be optionally substituted an example of an aralkyl group is benzyl and examples of nitrogen heterocyclic groups are pyridyl, morpholino and piperazyl. Specific compounds of the class are trimethylamine borane, dimethylamine borane, pyridine borane, cyclohexylamino borane, morpholine borane or

piperazine borane. Methods for the production of such boranes are described in articles by Burg et al., *J.A.C.S. 59*, 1937, 785–787 and Taylor et al., *J.A.C.S. 77*, 1955, 1506. In general terms, the compounds may be prepared by reacting sodium borohydride, $NaBH_4$, with a hydrochloride salt of an amide of the formula $R_1R_2R_3N$.

In a modification of the invention, there may be used, instead of an amine-borane, a precursor for an amine-borane as referred to above.

Advantageously, the reducing agent is slightly in molar excess. Typically, a color change is noted when the finely divided metal is obtained from the reducing reaction.

To this dispersion is added from about 100 to 150 percent by volume of an organic solvent which is substantially immiscible with water. Toluene is a preferred organic solvent, but benzene, cyclohexane, hexane, xylene, ether, chloroform, etc. can be used.

The mixture of the water solution and water immiscible solvent is acidified to a pH below 7 by adding an acid. Any water soluble acid, either organic or mineral, can be used. However, a convenient acid is hydrochloric of about 1.0 N concentration which is added in sufficient quantity to convert the acid salt to its acid such as sodium myristate to myristic acid, preferably to a pH below about 4.0.

The colloidal metal is extracted into the immiscible solvent phase, usually along with the fatty acid. The aqueous phase containing the water soluble reaction products of the reduction, etc. is separated from the immiscible solvent phase typically by decanting.

Water soluble, as used herein, is understood to mean capable of mixing with water at about 20° C. to form a homogeneous mixture (solution) and having about 1 part to about 100 parts by weight solvent needed to dissolve 1 part by weight substance (solute).

Immiscible solvent, as used herein, describes a liquid which will dissolve a substance from a solution with which it does not mix to form a homogeneous mixture (solution) at about 20° C.

The colloidal metal, prepared according to the invention, can be used in preparing a receiving layer for use in the diffusion transfer process. The receiving element is prepared by coating the solvent dispersion on a suitable support. In a particularly advantageous embodiment, the nuclei are coated at about 1 to about 200 micrograms per square foot.

The receiving element as described above is used advantageously to provide a photographic print having an image in the receiving layer on a support. The image is obtained by the diffusion transfer process and is formed in the receiving layer which comprises a binder and the metal nuclei of our invention. Particularly good results are obtained using palladium and platinum nuclei.

The following examples are included for a further understanding of the invention:

Example 1.—An example of nuclei preparation

Silver nitrate 0.340 g. ($2\times10^{-3}$ moles) dissolved in 25 ml. of water is poured into 100 ml. of a 2% sodium myristate solution in water. A transient precipitate, presumably silver myristate, forms but redissolves within a few minutes. The pH of this solution is 9.8–10.0. To this is added a solution of 0.110 g. ($2\times10^{-3}$ moles) $KBH_4$ dissolved in 25 ml. water; a red-brown color of finely divided silver appears instantly. To this dispersion, which now contains reduced silver peptized by sodium myristate, is added an equal volume of toluene, which forms a layer atop the aqueous dispersion. The mixture is stirred, 1.0 N HCl is added dropwise, and addition continues until the aqueous phase is clear and the silver, peptized now by myristate acid, is extracted into the toluene phase. Final pH of the aqueous layer is 3.5–3.9. This dispersion is now diluted with toluene, and shows the yellow brown color typical of colloidal silver. Acetone produces no noticeable coagulation, but instant coagulation occurs when a small amount of dispersion is added to methanol or ethanol.



Example 2.—Stability of nuclei

The dispersion is allowed to stand and electronmicrographs are made at intervals. They show that the dispersion is stable for at least ten days. The average particle size is 60 A., with most of the particles in the 47–77 A. size range.

Example 3.—Coating containing silver nuclei

These nuclei are then coated in a mixture of silver behenate (.048 M), behenic acid (.048 M), binaphthol (.048 M) and phthalazinone (.024 M). The coatings are heated to 110° C. for varying times. Small amounts of nuclei (.02–.04 mg./ft.$^2$) accelerate the rate of silver reduction markedly compared to the control with no nuclei. Concentrations of 0.4–0.5 mg./ft.$^2$ accelerate the rate further. At coverages of 0.5–0.9 mg./ft.$^2$, no further acceleration is observed.

Example 4.—Coating containing Pd nuclei

To a solution containing 0.653 g. ($2\times10^{-3}$ moles) $K_2PdCl_4$ is added 25 ml. of a 4% sodium myristate solution. To this slightly cloudy mixture is added 0.11 g. ($2\times10^{-3}$ moles) $KBH_4$ dissolved in 25 ml. water. Reduction to metallic Pd takes place immediately. Toluene, followed by dropwise addition of HCl causes the Pd to be extracted into the non-aqueous layer (as in Example 1). Coatings are then made as described in Example 3, except colloidal Pd is added in place of colloidal Ag. A comparison of the control coating (no nuclei) with the nucleated coatings shows that the rate of silver development increases with increased Pd coverage, and demonstrates that dry physical development, like conventional development, is catalyzed by palladium.

Example 5.—Reducing agents used with $K_2PdCl_4$

Example 4 is repeated using hypophosphite, stannous chloride, formaldehyde and hydroxylamine reducing agents with satisfactory results.

Example 6.—Coating containing noble metal nuclei

Example 4 is repeated using $PdCl_2$, $Na_2PtCl_6\cdot6H_2O$, $RuCl_3$, $RhCl_3\cdot4H_2O$ and $KAuCl_4$ with satisfactory results.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A composition of matter comprising a stable suspension of colloidal noble metal and a peptizing amount of a fatty acid having 10 to 22 carbon atoms in a substantially non-aqueous water-immiscible organic solvent medium, said colloidal noble metal having an average particle size of about 47 to about 300 A.

2. A composition of claim 1 in which said metal is silver.

3. A composition of claim 1 in which said metal is palladium.

4. A composition of claim 1 in which said solvent is toluene.

**References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 3,413,240 | 11/1968 | Short | 106—1 |
| 3,434,877 | 3/1969 | Degenkolb et al. | 106—1 |
| 3,470,019 | 9/1969 | Steele | 106—1 |
| 3,635,761 | 1/1972 | Hagg et al. | 106—1 |
| 3,511,660 | 5/1970 | Stevens et al. | 96—84 M |


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