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3,404,093

FLUORESCENT COMPOSITION FOR MAGNETIC PARTICLE INSPECTION

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ABSTRACT OF THE DISCLOSURE

A fluorescent magnetic material for use in non-destructive methods of testing ferromagnetic work pieces, comprising discrete magnetic particles coated with a thermoplastic resin containing a fluorescent dye, preferably in combination with an opacifier having a cascading effect in combination with said dye, the coated particles having an average particle size preferably of not over about 5 microns maximum dimension. The method of coating includes dissolving a thermoplastic resin and a fluoragent in a water-miscible organic solvent to form a solution thereof, separately forming a water dispersion of highly divided magnetic particles, and then adding the solution to the water dispersion with thorough mixing until the resin and fluoragent are thrown out of solution, whereby the magnetic particles become coated with a sticky, adherent coating of the resin and fluoragent. The water dispersion of magnetic particles is formed under conditions of high shear. The thermoplastic resin, which is preferably a melamine-toluene sulfonamide-formaldehyde resin, is insoluble in water and therefore precipitates out upon dilution of the resin-fluoragent solution with the water of the water dispersion magnetic particles.

This invention relates to a fluorescent composition for magnetic particle inspection and to a method of making the same.

Non-destructive methods of testing structures of ferromagnetic material (herein sometimes referred to as "test pieces," or "work pieces"), by the use of fluorescent magnetic particles have been described in Patents Nos. 2,267,999, 2,936,287 and others. Such methods involve the inspection of the test piece in the substantial absence of visible light but under filtered ultraviolet light, usually referred to as "Black Light." One of the advantages of using fluorescent magnetic particles, as compared with magnetic particles having only their natural visible coloration, is that there is a greatly increased contrast between the fluorescent magnetic particles and the background of the test piece, thereby giving a greatly increased sensitivity in the inspection of the surface for indications of surface discontinuities, flaws and the like.

Heretofore used fluorescent compositions, however, have been relatively expensive and difficult to manufacture. In order for the fluorescent composition to be satisfactory for use in magnetic particle inspection methods the composition must possess a high order of visible brightness when viewed under Black Light and the particles making up the fluorescent composition must be relatively resistant to physical change as a result of rubbing forces tending to separate the fluorescent coating from the magnetic particles, during, for instance, the agitation of baths containing suspensions of such fluorescent-coated magnetic particles. Also, there is the problem of separation of the fluorescent pigment coating from the magnetic particle during grinding of the composition to obtain the very fine particle size desired in the finished product.

It is therefore an important object of the present invention to provide an improved method of bonding a fluo-

rescent coating to magnetic particles so as to increase the resistance of the particles to separation of the coating from the particles during grinding thereof and during use of the composition when suspended in liquids subjected to severe agitation in agitated and circulated systems.

It is a further important object of this invention to provide fluorescent compositions for magnetic particle inspection that have increased fluorescent brightness and therefore a higher degree of visibility; that permit of a wider choice of colors at lower cost and with greater ease of manufacture.

Other and further important objects of this invention will become apparent from the following description and appended claims.

In the method of making fluorescent compositions according to my present invention, a thermoplastic resinous fluorescent coating is applied to the magnetic cores, as the initial, uncoated magnetic particles are termed herein. In forming the coating, a solvent is used for dissolving the thermoplastic resin that is relatively miscible with water and that can be removed from the coatings after application to the magnetic cores by the simple step of suspending and agitating the coated particles in water. This step simultaneously effects the precipitation on the cores of the resin in a sticky form. Such stickiness is due to the presence of solvent in the resin coating and become less as the solvent is leached out into the water. Any residual traces of solvent in the coated particles are removed by washing, after which the coated particles are dried and ground. The removal of the residual solvent from the coated particles leaves the resin coating of the particles firmly adherent to the magnetic cores as a relatively hard and high melting point, solvent-free resin. Thermoplastic resins are chosen that have softening points of at least 100° C. or over, so that there is no tendency of the resin-coated particles to become agglomerated in the grinding thereof due to the generation of heat in the grinding operation.

In the coating of the magnetic cores the thermoplastic resin and the fluoragents may be dissolved separately in the water-miscible solvent to be used, or the resin and the fluoragents may first be combined into a pigment form, in accordance with the method described in Patent No. 2,938,873, or by any suitable method. Whether the thermoplastic resin and the fluoragents are separately dissolved in the solvent or a pre-formed pigment consisting essentially of the thermoplastic resin and the fluoragents in a solvated state in the resin, the result is the same. Since, however, fluorescent thermoplastic resin pigments are available on the market that are suitable for use in accordance with my invention, it is usually less expensive and less trouble to use the available fluorescent thermoplastic resin pigments than to prepare them separately.

The term "fluoragent" is used herein to designate a substance that is capable of emitting visible light under invisible fluorescigenous radiation, such as "Black Light." Preferably, two or more fluoragents are used in the resinous coating for the magnetic cores in making my fluorescent composition. At least one of the fluoragents used is a fluorescent dye capable by itself of emitting visible light when subjected to fluorescigenous radiation to exhibit a color brightness that is more than twice that which would be due to reflectance alone, as in the case of a visible dye. The other of the plurality of fluoragents may be also a fluorescent dye, recognized as such, or it may be a substance having a different absorption-emission curve from that of the principal fluorescent dye and capable of exhibiting a "cascading effect" therewith. The term "cascading" is used in the sense in which it is used in Patent

No. 2,920,203, and for a further explanation of the term reference is made to that patent.

Instead of using a second, or additional fluorescent dye to obtain the cascading effect desired, a substance may be used that is not usually termed a fluorescent dye, but which exhibits the property of absorption of rays in the ultraviolet region, with emission of additional visible light over and above what would be reflected if the substance were subjected to visible light radiation only. The term "opacifier" has been applied to this second, or additional, fluoragent, since it has the property of being relatively opaque to ultraviolet light, that is, capable of absorbing ultraviolet light and re-emitting light rays in the visible range.

While the proportions of components of the fluorescent composition of my invention are relatively critical within rather broad limits, variations in proportions are entirely dependent upon the results sought to be achieved. In general, equal parts by weight of the magnetic core material and of the coating material may be used, but the proportion may be varied between two parts of the core material to one part of the coating material and one part of the core material to one and one-half parts of the coating material, by weight. The amount of fluoragents in the coating composition should not exceed that which is capable of being entirely dissolved, or solvated, in the resin. In general, from 0.5 to 5.0% of fluoragents may be used based upon the weight of the thermoplastic resin in the coating composition, with the opacifier, if one is used, present in the proper proportion to give a maximum cascading effect with the fluorescent dye used as the principal fluorescent color.

The following examples, giving general and specific formulae and procedures, will serve as illustrations of how my invention can be practiced to best advantage. It will be understood, however, that the examples are by way of illustration only and are not by way of limitation upon the scope of my invention.

Example I (General)

Formula:	Parts by weight
Magnetic powder -----	100.
Resin-fluorescent dye-opacifier mixture -----	70 to 100.
Organic solvent -----	300 or q.s. to dissolve mixture.
Water -----	3400.

Procedure:

(1) The resin, fluorescent dye and opacifier, either as separate components or as an admixture in which the fluorescent dye and opacifier are present in solvated state in the resin, are dissolved in the organic solvent to form a solution thereof.

(2) The magnetic powder is added to water, in the proportion of 100 parts of magnetic powder to 3400 parts of water, in a colloid mill.

(3) The colloid mill is run at 1/3 its rated speed for 15 minutes during which time the mill clearance is reduced from 0.020" to 0.005".

(4) Clearance is then increased to 0.030" and solution (1) is dumped in.

(5) The colloid mill is run for an additional period of 15 minutes at the same speed.

(6) The contents of the colloid mill are drained out and the dispersion run into a filter press, wherein the press cake is washed with clear water to remove all residual organic solvent from the filter cake.

(7) The filter cake from the press filter is added, along with water, to a ball mill wherein the size of the particles of coated magnetic material is reduced to an average of not over 5 microns.

(8) The ball-milled mass is then filtered to separate the ground powder and the latter dried in a low temperature oven.

The resulting dried powder comprises discrete magnetic particles coated with an adherent solvent-free resin film having solvated therein a fluorescent dye and an opacifier having a cascading effect with respect to said dye. The "cascading effect" results in an enhanced fluorescent brightness of color.

The coated magnetic material prepared in accordance with my invention has the following properties and characteristics:

(1) A brightness on a Fischer spectrophotometer twice, and usually two and one-half times, the brightness under filtered ultra-violet light (black light) of the fluorescent dye, by itself, used in the material;

(2) A capability to find at least 10 and usually 15 "indications" on a test wheel. The test wheel is a steel wheel that is circumferentially magnetized and provided with a plurality of transverse holes (bores) positioned at progressively greater distances radially inwardly of the periphery of the wheel to simulate defects in a workpiece. An acceptable fluorescent magnetic particle finds up to about 7 indications on such a wheel;

(3) A magnetic reading of 30, and usually about 40. Such magnetic reading is determined with the powder as the core in an electromagnetic coupling having a unity reading with air only as the core;

(4) Very poor oil durability in terms of mechanical stability against attrition or loss in weight of the individual particles when agitated in oil; but

(5) Good water durability or resistance to physical change and dye or opacifier when agitated in water containing a wetting agent as the bath.

Items 4 and 5 show that the fluorescent composition of my invention is not well adapted for use in oily vehicles often used for suspending magnetic particles but is especially well adapted for suspension in water as a water suspension for magnetic particle testing.

Suitable thermoplastic resins that can be used in Example I are the following:

Amino-triazine-sulfonamide-aldehyde resins specifically, melamine - sulfonamide-formaldehyde; benzoguanamine-sulfonamide-formaldehyde and other thermoplastic resins of Patent No. 2,938,873.

Polystyrene resins, water-white or transparent.

Terpene resins.

Zinc resinsates, i.e., zinc- or zinc-calcium resinsates that are permanently refusable and have melting points of above about 100° C. (capillary tube). As examples of suitable fluorescent dyes, the following are named:

Rhodamines (xanthenes); e.g., rhodamine B Extra; rhodamine 6 GDN Extra; xylene red

Naphthalimides; e.g. brilliant yellow (6 G base); (4 N-butylamino) 1,8 naphthal N-butylimide

Coumarins; e.g. dimethyl amino coumarin; 4 methyl 7 diethyl amino coumarin

Stilbenes; e.g. p, p' di [p'' (p'' amino benzoylamino) benzoylamino] stilbene o,o' di [sodium sulfonate]

Fluorols (General Aniline & Chemical Co.); e.g. Fluorol 7GA, Fluorol 5GA.

Azines; e.g. 2 hydroxy 1, naphthaldazine

As examples of suitable opacifiers, the following are named:

Multi-ring benzenoid hydrocarbons; e.g. anthracene (C₆H₄ (CH₂) C₆H₄) pyrene (C₁₆H₁₀)

fluoranthene (C₁₆H₁₀)

Fused polycyclic hydrocarbons

Pentalene

Ovalene

In general, all materials that fluoresce blue-white and cascade the fluorescent dyes have proven satisfactory. There are thirty five of these materials, the structural formulae of which are listed in the Chemical Rubber Handbook, 45th Edition, pp. C-11 and C-12.

Examples of suitable magnetic materials are the following:

Iron particles; e.g. carbonyl iron (5 micron particle size)
Iron oxides; e.g. gamma Fe_2O_3 ; natural and synthetic magnetite, Fe_3O_4 ; and mixtures thereof. The respective mean particle sizes of gamma Fe_2O_3 , natural magnetite and synthetic magnetite are suitably: less than 1 micron, about 3 microns and about 6 microns.

Examples of suitable water-miscible organic solvents are the following:

N,N-dimethyl formamide (DMF)
Dimethyl sulfoxide (DMSO)
N-methyl-2-pyrrolidone
Acetone (dimethyl ketone)
Pyrazine
Piperidine
Dioxane
Morpholine
Pyridine
Azidine
Dimethyl acetamide

Any of the foregoing components can be substituted for the corresponding generally named components of the Formula of Example I in like amounts to those therein specified with generally satisfactory results.

Example II (Specific)

Formula:	Parts by weight
Magnetic powder, as a mixture of gamma Fe_2O_3 synthetic and natural magnetite, Fe_3O_4 (average particle size less than 6 microns) -----	25
Resin, melamine-sulfonamide-aldehyde-----	20
Fluorescent dye, Fluorol 7GA-----	1
Opacifier, fluoranthene -----	4
Organic solvent, dimethyl formamide-----	75
Water -----	750-1000

In place of the melamine-sulfonamide-formaldehyde resin in Example II, a thermoplastic zinc- or zinc-calcium resinate such as described in Patents Nos. 2,346,992 and 2,346,993, respectively, can be substituted, without change in the other components for the amounts of the resin components given in said example. A zinc resinate is available on the market under the trademark "Zitro" of Heyden Newport Chemical Company, a division of Tennessee Gas Transmission Company.

Procedure.—The resin, dye and opacifier are dissolved in the dimethyl formamide to form a solution thereof. The magnetic powder is separately milled in water to a particle size of less than 5 microns, if necessary. The separately formed resin-solvent-dye-solution is then added to the water suspension of the magnetic powder in the mill, and agitation is continued until a sample removed from the mill, after washing with water and drying, shows maximum fluorescent brightness. The entire mass is then dumped, filtered, and the filter cake washed and dried. The resulting particles comprise the magnetic cores and resinous coatings in approximately equal proportions by weight.

The final fluorescent composition, prepared as described above, can be made into a concentrated aqueous paste of the fluorescent magnetic particles for dilution when used, or can be sold as a dry powder for use in magnetic particle testing or for other purposes, such as for magnetic inks to identify checking accounts and the like. When made into a water suspension for magnetic particle inspection of magnetizable test pieces for surface discontinuities, the usual concentration is approximately $\frac{1}{8}$ oz. of the fluorescent composition per gal. of water, but the concentration can vary between $\frac{1}{16}$ and $\frac{1}{4}$ oz. per gal.

My fluorescent composition has the advantage of being physically resistant to fragmentation during agitation and circulation of the water suspension of the fluorescent mag-

netic particles and also resistant to bleeding of color into the water of the suspension. Additionally, because of the cascading effect, the composition has as good, if not better, brightness than heretofore known fluorescent magnetic particle compositions. In general, it is less expensive to manufacture and presents fewer manufacturing problems, especially when a pre-formed resin-dye-opacifier, such as a daylight fluorescent color pigment, is used. Prior to my discovery of the feasibility of using organic solvents that have solvent action toward all of the thermoplastic resins, fluorescent dyes and opacifiers used in making my fluorescent composition and that are miscible with water, no method was available to the best of my knowledge, for making a satisfactory fluorescent composition for magnetic particle inspection from the individual components, or from already formed daylight fluorescent resinous pigments.

The latter pigments are available on the market under the proprietary names, "Day-Glo," of Switzer Brothers, Inc., and "Hy Viz," of Lawter Chemical Co.

It will be understood that modifications and variations may be effected without departing from the scope of the novel concepts of the present invention.

I claim as my invention:

1. The method of making a fluorescent magnetic material in particulate form, which comprises:

dissolving a thermoplastic resin and a fluoragent in a water-miscible organic solvent to form a solution of said resin and fluoragent,

separately forming a water dispersion of finely divided magnetic particles, and

adding said solution to said water dispersion with thorough mixing until said resin and fluoragent are thrown out of solution,

whereby said magnetic particles become coated with a sticky, adherent coating of said resin and fluoragent.

2. The method as defined in claim 1, wherein

said fluoragent is initially in a solvated state in said resin, and

said water dispersion of magnetic particles is formed under conditions of high shear.

3. The method as defined in claim 1, wherein

said fluoragent includes a dye and opacifier, and

said opacifier is a multi-ring benzenoid hydrocarbon having absorption in the ultraviolet range and having a cascading effect upon the fluorescent dye.

4. The method of making a fluorescent magnetic material which comprises the steps of:

dissolving a mixture of a water insoluble thermoplastic resin, a fluorescent dye and an opacifier having a cascading effect with respect to said dye in a water-miscible organic solvent to form a solution of said mixture,

separately forming a water suspension of dispersed finely ground particles of magnetic material of an average particle size less than 5 microns, adding with agitation said solution of said mixture to said suspension in such proportions of said solution and said water suspension as to effect a precipitation of said mixture upon said magnetic particles to coat the same while said mixture is in a sticky, adhesive condition due to the presence of residual solvent therein, and

continuing agitation until the coating of said particles and the removal of said residual solvent from said coating have been substantially completed,

whereby there results a mass of discrete magnetic particles coated with a substantially solvent-free resin containing said fluorescent dye and opacifier and having a brightness exceeding that due to the fluorescent brightness of said dye alone.

5. The method as defined in claim 4, wherein said organic solvent is dimethyl formamide.

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6. The method as defined in claim 4, wherein, said organic solvent is dimethyl-sulfoxide.

7. The method as defined in claim 4, wherein said thermoplastic resin is a triazine-sulfonamide-formaldehyde resin.

8. The method as defined in claim 4, wherein said thermoplastic resin is a zinc resinate.

9. The method as defined in claim 4, wherein said opacifier is fluoranthene.

10. The method as defined in claim 4, wherein said opacifier is anthracene.

11. The method as defined in claim 4, wherein said thermoplastic resin is a melamine-sulfonamide-formaldehyde condensation product, said organic solvent is dimethyl formamide, said dye is a naphthalimide, and said opacifier is fluoroanthene.

12. A composition of matter comprising discrete magnetic particles coated with a thermoplastic resin containing a fluorescent dye and an opacifier selected from the group consisting of fluorescent multi-ring benzenoid hydrocarbons, pyrene, fluoranthene and fluorescent fused polycyclic hydrocarbons, said opacifier having a cascading effect in combination with said dye, said coated particles having an average particle size of not over about 5 microns.

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13. A composition as defined in claim 12, wherein the thermoplastic resin is a triazine-sulfonamide-formaldehyde resin.

14. A composition as defined in claim 12, wherein said opacifier is fluoranthene.

15. A composition as defined in claim 12, wherein said magnetic particles comprise a mixture of gamma Fe_2O_3 and natural magnetite, Fe_3O_4 , said thermoplastic resin is a melamine-sulfonamide-formaldehyde resin and said opacifier is fluoranthene.

16. An aqueous suspension of the composition as defined in claim 12.

17. An aqueous suspension of the composition as defined in claim 15.

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