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Trimble et al.

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[54] **MEANS AND METHOD FOR CREATING A VISIBLE DISPLAY UTILIZING HIGH SENSITIVITY MAGNETOCHEMICAL PARTICLES**

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[22] Filed: **Aug. 26, 1974**

[21] Appl. No.: **500,271**

Related U.S. Application Data

[62] Division of Ser. No. 210,077, Dec. 20, 1971, Pat. No. 3,882,507.

[52] **U.S. Cl.**..... **346/74.1;** 29/DIG. 95; 117/100 M; 148/105; 360/55; 360/131

[51] **Int. Cl.²**..... **G03G 19/00;** G11B 5/84; G01D 15/34

[58] **Field of Search** ..... 360/131, 137, 55, 114, 360/116, 56, 113; 324/43, 47; 346/74.1; 29/DIG. 95; 117/100 M; 148/31.5, 105

[56] **References Cited**

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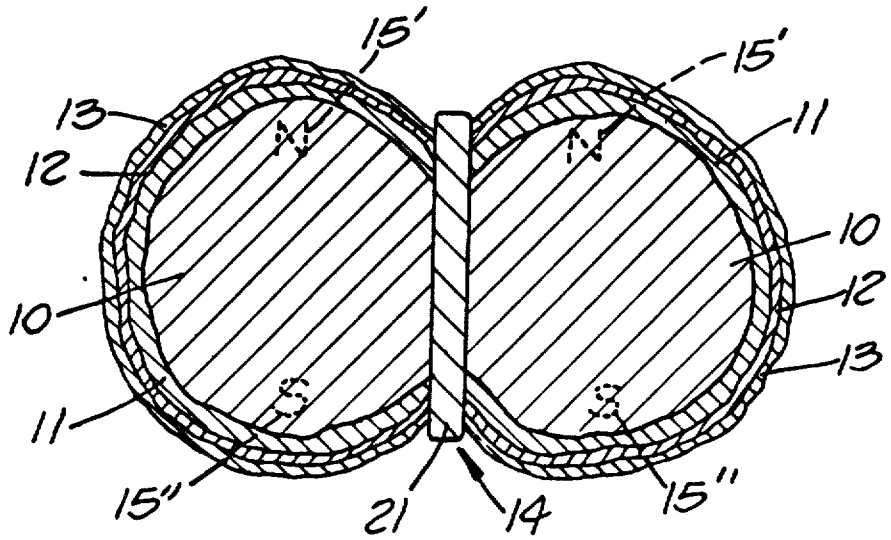
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Attorney, Agent, or Firm—Robert M. McManigal

[57] **ABSTRACT**

Improved means and method for creating a visible display utilizing magnetochemical particles that respond to a magnetic field by exposing an interface capable of reacting chemically with a surrounding chemical environment to provide an immediately visible change in color. Waterphase droplets in a carrier medium provide an envelope for the chemical and contained particles. The particles have a high sensitivity to magnetic fields obtained by a unique structure which utilizes two masses of ferromagnetic materials usually in spherical form, and in which each has a core of magnetostrictive material with properties common to hard magnetic materials. Each core is coated with a metallic material capable of reacting upon exposure to the chemical environment to produce a visible color, but which is normally shielded and prevented from reacting by an overcoating of a brittle material. The two masses are relatively oriented and physically attached with their magnetizable axes in parallel relation, whereby upon subjection to a magnetic field, magnetic poles will be induced which produce repulsive forces for assisting in the rupture of the particle. Thus, when the particle is exposed to a magnetic field pulse, three forces influence its performance. The force generated by magnetostriction provides motion that acts to loosen the bond between the brittle frangible coating and the chemically reactive layer; the induction of adjacent like poles in the attached spheres generates a force of repulsion which, added to the magnetostrictive force, ruptures the frangible physical attachment and exposes the color forming metal to the surrounding chemical environment; the hard magnetic quality of the mass material results in the formation of two permanent magnets such that the force of repulsion persists following induction to complete the rupture started by the triggering pulse.

6 Claims, 5 Drawing Figures



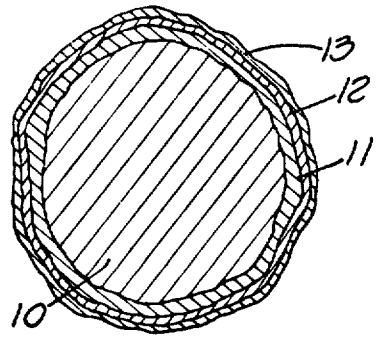


FIG. 1.

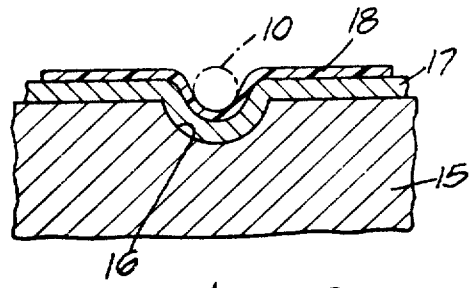


FIG. 2.

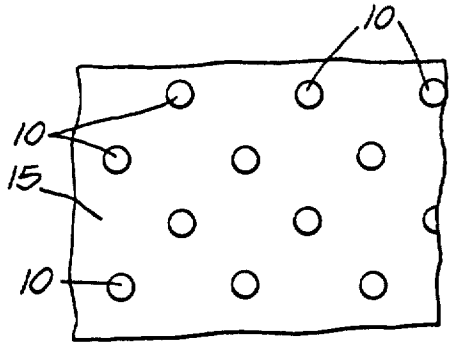


FIG. 3.

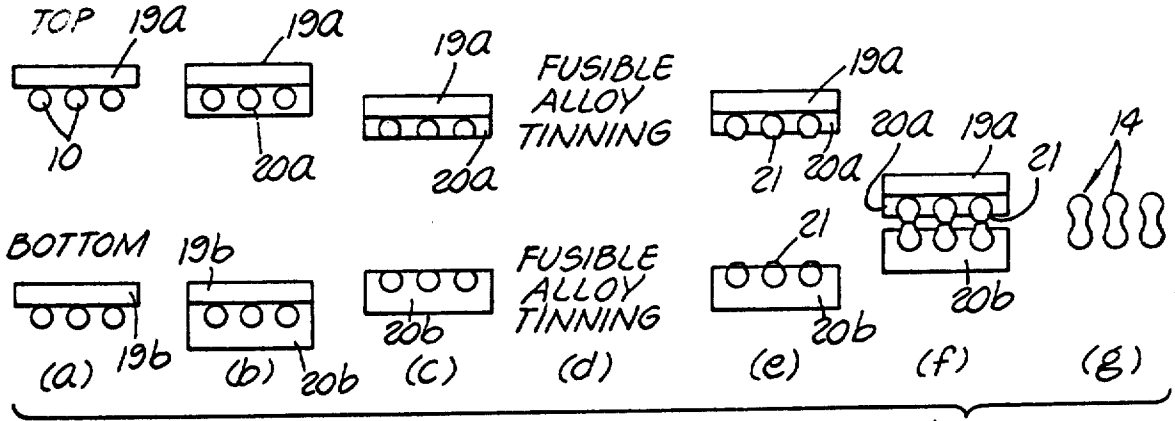


FIG. 4.

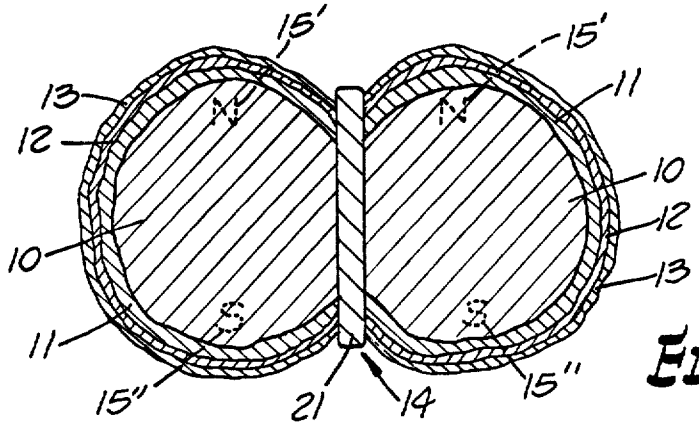


FIG. 5.

MEANS AND METHOD FOR CREATING A VISIBLE DISPLAY UTILIZING HIGH SENSITIVITY MAGNETOCHEMICAL PARTICLES

This is a division of application Ser. No. 210,077, filed Dec. 20, 1971, now U.S. Pat. No. 3,882,507.

BACKGROUND OF THE INVENTION

The present invention is broadly concerned with the creation of a visible display in response to the magnetic stimulation of magnetochemical particles.

Heretofore, the use of magnetic fields as a means of triggering chemical activity to provide a visible change has been generally known from U.S. Pat. No. 3,281,669. It has been also known from U.S. Pat. No. 3,512,169 to utilize such means generally for creating visible displays in color. In both of these patents, the creation of the visible display was dependent upon magnetostrictive size change induced in certain materials by a magnetic field. The material was selected with provision for overplating such that contact with a colorless chemical environment would bring about a chemical change to form color, and it was coated with a frangible protective film that could be severed by sufficient magnetostrictive size change, so that exposure to a magnetic field resulted in the formation of a visible color. The change in size of the magnetostrictive materials in many instances was found to be insufficient to cause rupture of the frangible protective film, when the magnetic field strength was reduced substantially below 1000 oersteds. To avoid borderline situations involving control of very thin frangible films and to increase sensitivity for response to magnetic field exposure, the present invention takes advantage of additional forces found to be available from a magnetic field. Thus, it has been found that the forces of repulsion between two like magnetic poles generated in two adjacent ferromagnetic materials by magnetic field exposure can augment the magnetostrictive forces and assist in triggering chemical activity in a surrounding chemical environment. The combination of magnetostrictive action and mutual repulsion of like poles has been found sufficiently effective to bring about chemical activity at field strengths in the order of 100 oersteds.

A mathematical estimation can be made to indicate the maximum force of repulsion that will result from magnetic field induction in adjacent magnetic materials. In general, the force increases with the square of the material radius and it increases as the physical configuration progresses from spheres to plates to rods. The force can act in tension, bending, or torsion to separate two attached magnetic materials. However, as the size of the material is substantially reduced and the performance of very tiny particles is considered, the occurrence of self demagnetization acts to offset mathematical estimations. In small magnetic materials, it is of uncertain and unpredictable magnitude.

For tiny ferromagnetic materials attached together and exposed to magnetizing pulses of a few micro seconds duration, it has been found that both magnetostrictive forces and mutual repulsion forces can be active in bringing about separation. However, inertia (overcome by the prolonged forces generated during a longer pulse) can prevent the materials from fully separating during the short exposure time and can delay the formation of a visible change in a surrounding chemical environment. To insure a complete break-away, it has been found desirable to use hard magnetic materials characterized by the ability to maintain a magnetic field following magnetization. Thus, the poles established through magnetic induction will maintain a portion of the strength induced in them and continue overcoming the inertia of the materials following the magnetizing pulse. To further enhance performance, the materials can be treated to bring into being a preferred direction of orientation with respect to the establishment of permanent magnetic fields, and these magnetic field directions can be aligned before material to material attachment.

A variety of substances known generally as hard magnetic materials may be used for this purpose, and tabulations of suitable materials and properties are to be found in the C. C. Van Nostrand publication (1961) "Ferromagnetism" by Dr. R. M. Bozorth, particularly in the table, pages 872 and 873. Other hard magnetic alloys and ceramics developed since 1961 are also applicable. A preferred direction of orientation can be established by heat treating and annealing in a magnetic field. The subsequent alignment of heat treated and annealed materials can be accomplished by suspending them in a directional magnetic field so that they can freely rotate to bring the preferred directions of orientation in line with the field direction. Magnetic materials so aligned can be attached with a suitable adhesive bond. This structure and its performance, with modifications to be discussed, is a main feature of the present invention, and although it will be referred to as the magnetochemical particle, it is understood to be a high sensitivity magnetochemical particle and a substantial improvement on the prior art.

SUMMARY OF THE INVENTION

The present invention relates generally to means and method for creating a visible display by means of magnetochemical particles, and in particular such particles as will respond to relatively low strength magnetic fields, and upon exposure thereto are capable of reacting with a chemical environment to bring about an immediately visible change.

In its broad concept, the objects of the present invention include:

a. The provision of means by which magnetic inductions from low field strength, short duration magnetic pulses are utilized to trigger a chemical reaction productive of a visual change in the area of the magnetic field application.

b. Provision of a magnetic field sensitive visual display technique responding to low field strength magnetic pulses by triggering the occurance of a chemical reaction to produce a visible change in the area of magnetic field application.

c. The provision of a magnetochemical particle consisting of attached magnetic materials capable of detachment when subjected to a magnetic field.

d. The provision of a magnetochemical particle comprising a pair of ferromagnetic materials aligned so that their preferred directions for magnetic field orientation are parallel, then joined together to preserve the orientation alignment.

e. The provision and use of a magnetochemical particle comprising magnetostrictive materials having properties characteristic of hard magnetic materials, each coated with a chemically reactive metal, suitably attached and suspended in a chemical environment

within which the metal would normally react but from which it is protected by a brittle relatively non-reactive continuous surface coating applied over the external surface. This brittle coating is selected to have the capability of being ruptured or rendered discontinuous in response to the forces generated by and between the magnetic materials under the influence of a magnetic field, thus allowing the chemically reactive metal to react with the chemical environment.

f. The embodiment of magnetochemical particles and a surrounding colorless but color-forming environment in droplet form in such a manner that the droplet size can be controlled to establish image resolution in an applied coating prepared by dispersing these droplets in a resinous carrier and applying the carrier to a surface.

g. Means for obtaining permanent visible images in color following exposure to a magnetic field substantially less than 1000 oersteds and in particular below 800 oersteds to improve upon the condition shown in FIG. 5 of the referenced U.S. Pat. No. 3,281,669.

h. Provision of magnetochemical particles capable of selectively triggering chemical reactions in response to different magnetic field pulse times and threshold levels.

i. Provision of unique means for preparing magnetochemical particles of the character referred to in the previously noted objectives.

j. The provision of method and means wherein a plurality of variable parameters can be selectively controlled, either individually or in combination, in order to obtain a variety of desirable effects in the creation of color displays.

k. The provision of an additive three color hard copy on film, paper, or plastic, wherein the colors are stimulated by magnetic means upon a real time basis.

l. Means for providing a coating that can be applied to a supporting medium to disclose the presence of a magnetic field whether present at the time of application or created later.

m. The provision of means for creating a visible discernible area coincident with a magnetizing action which produces a magnetized area.

n. Means for providing coatings on thin supporting media that may be positioned against or bonded to and later removed from surfaces believed to contain magnetic fields so that a visual image can be produced on or within the applied coating which, if removed can be separately inspected by either reflection or transmission viewing.

o. The provision of a visible image in the areas of magnetic fields, wherein the visual density or image intensity is proportional to the intensity of the magnetic field.

p. The provision of a visible image of magnetic fields with a resolution equal to the magnetic recording resolution.

Further objects and advantages of the invention will be brought out in the following part of the specification, wherein detailed description is for the purpose of fully disclosing an embodiment of the invention without placing limitations thereon.

BRIEF DESCRIPTION OF THE DRAWINGS

Referring to the accompanying drawings, which are for illustrative purposes only:

FIG. **1** is an enlarged cross-sectional view diagrammatically illustrating a sphere constructed according to the present invention;

FIG. **2** is a cross sectional view of a dimpled plate structure as utilized in the preparation of magnetochemical particles according to the present invention;

FIG. **3** is a plan view of a dimpled plate showing the distribution pattern of spheres thereon;

FIG. **4** is a view diagrammatically illustrating successive steps for the alignment of spheres and their attachment to provide the respective particles; and

FIG. **5** is an enlarged view diagrammatically disclosing a particle composed of two joined spheres, according to the present invention.

DESCRIPTION OF A PREFERRED EMBODIMENT

Referring more specifically to the drawings, there is shown in FIG. **1**, a mass of ferromagnetic material in the form of a sphere as generally indicated by the numeral **10**, which forms a basic component of the present invention. The preparation, treatment, and use of these spheres according to the present invention will now be explained in detail.

Magnetic Material Selection

A number of magnetic materials can be employed in the construction of the spheres **10**. Commercially available alloys containing cobalt, iron, aluminum, nickel and copper and known as Alnico alloys have been used as have those containing iron, cobalt, and vanadium and known to the trade as Vicalloy. A particular alloy which has been used successfully is one known in the trade as Alnico 5, which has a composition in addition to iron of 24 percent cobalt, 14 percent nickel, 8 percent aluminum and 3 percent copper. The characteristics of this alloy as indicated by Dr. Bozorth show that a coercive force of 600 oersteds is attained following a magnetizing field of approximately 450 oersteds, and that lower residual fields suitable for mutual repulsion purposes are attained with lower magnetic induction levels. Because of self demagnetization, it is the prevailing belief that these characteristics are greatly diminished when a small particle of the alloy is being considered.

Magnetic Material Preparation

Magnetic alloys are often prepared in ingot form. The metal can be melted and sprayed into an inert atmosphere so that tiny spheres are formed without substantial change in the alloy composition. The size of the spheres can be controlled by the several parameters well known and in use in the metalizing art. Following cooling, the spheres are mechanically separated to isolate the desired size range by using known techniques such as vibration, rotation through tubes, sieving, and the like. For the purpose of the present invention, spheres in the 20–30 micron diameter size range were selected for use, and were separated from the metalizing yield by mechanical sieving. This choice of size is purely optional and based upon certain tooling as will be hereinafter discussed. Spheres as small as 5 microns in diameter and as large as 100 microns in size were used. Larger sizes are equally suitable; however, the AC fields required to erase these larger spheres become excessive.

The selected spheres are heat treated and annealed in a magnetic field to create within each a preferred orientation with respect to magnetic field direction. The

exact procedure depends upon the alloy that is used. If the alloy is ductile, such as the above mentioned Vicalloy, then physical hot or cold working can be substituted for heat treating and annealing. In such case, the spheres are cold rolled to form elliptical plates that display a preferred direction of orientation to an applied magnetic field, for example, parallel to the long axis of the ellipse. A suitable technique for the Alnico 5 alloy involves packing the spheres to minimize caking, then heating to a temperature of substantially 1200° to 1300°C. for 1–5 minutes in a dry hydrogen atmopshere. The spheres are then cooled to a temperature of 700°C. in 2 minutes at a rate of approximately 300°C. per minute. The cooling is conducted in a 1000 oersted magnetic field having a single direction through the mass of spheres. The magnetic field application and cooling rate below 700° C. is not critical. The spheres are then aged for eight hours at a temperature of approximately 600°C., which may vary by 10°C. in an atmosphere of argon or hydrogen. An evaluation of heat treated and annealed Alnico 5 spheres showed that in addition to an improvement in magnetostrictive properties, the directional orientation increased the residual magnetic field following induction by a factor between 3 and 4.

Magnetic Material Plating

Although the metals making up these heat treated spheres will react with a selected chemical environment to form colored products, the reaction rate tends to be slow unless a strong chemical environment is used to dissolve metal from the alloy. To increase the rate of chemical reaction, a thin film, number **11,** is formed around each sphere by electroless plating with any one of several ductile metals capable of forming colored salts, such as iron, nickel, or cobalt. These metals are readily dissolved by a dilute suitably proportioned chemical environment, as described in U.S. Pat. No. 3,281,669. For the purposes of the present invention, iron was selected as the color forming metal; and a film thickness up to 1 micron was found to be suitable, when deposited from an electroless plating bath compounded and used as shown in the following Table 1. Other application techniques, such as vapor deposition and metal spraying can also be used to provide thin metal films, but electroless plating is preferred.

A frangible protective coating, number **12,** is next applied over the iron layer by using electroless plating techniques. Although brittle substances like antimony can be used as described in the above referenced patent, very good results have been obtained also by applying a thin film of copper and/or copper oxide. The copper was applied by using the well-known Fehling's reaction which, in the absence of an oxygen-getter and when used as shown in the following Table 2, deposits a brittle film that is a mixture of copper and cuprous oxide. The adhesion of this film to iron and other metals is poor and it can be substantially destroyed by the magnetostrictive size change, when the sphere is magnetized. A film, one to one-and-one-half microns in thickness, provides resistance to the color forming chemicals contained in the environment in which the magnetochemical particle is suspended; however, for the reasons discussed below, an additional protective layer **13** of tin or nickel-tin is used. This frangible coating, number **12,** will hereinafter be referred to as copper, although it will be understood that it is actually the metal oxide mixture obtained by plating as described above. Although specific plating formulas have been given in Table 1 and Table 2, it is to be understood that other suitably proportioned electroless plating baths capable of depositing these metals may be used in accordance with the broad concepts of the present inventions.

TABLE 1

ELECTROLESS IRON	
Ferrous Sulfate ($FeSO_4$)	20 grams
Sodium Citrate ($Na_3C_6H_5O_7.2H_2O$)	60 grams
Water to make	1.0 liter
Add just prior to use:	
Ammonium Hydroxide (NH_4OH)	30 ml
Sodium Borohydride ($Na\ BH_4$)	2 grams
Temperature	60°C.
Plating Time	9 minutes

TABLE 2

ELECTROLESS COPPER	
Rochelle Salts ($KNaC_4H_4O_6.4H_2O$)	170.00 grams
Sodium Hydroxide ($NaOH$)	50.00 grams
Copper Sulfate ($Cu\ SO_4.5H_2O$)	37.00 grams
Formaldehyde (CH_2O 37% Volume)	200.0 ml
Water to make	1200 ml
Temperature	50°C.
Plating Time	7 minutes

The copper surface has a red-orange reflection, when viewed in white light; and since this can impart a tint to a transparent medium containing the spheres, the coating, number **13,** of tin is contact plated on the copper surfaces to minimize this tint. If the spheres are immersed in a 2 percent sodium stannate solution with aluminum at 65° to 80°C. a small amount of tin will be plated on the copper. This tin film is bright, highly reflective, and masks the copper tint. The presence of the tin film does not affect the magnetochemical particle preparation techniques to be described nor the particle performance characteristics although it does provide additional resistance to penetration of color forming chemicals. Films of nickel-tin alloys are equally effective in brightening the sphere surfaces and these also provide resistance to penetration of color forming chemicals. As deposited from the bath of Table 3, nickel-tin films are frangible as well as resistant and can be used over a very thin layer of copper to provide equal protection, as indicated in FIG. **1.** Brittle plastic films such as Acryloid A-11 deposited by solvent evaporation will provide resistance to the penetration of the color forming chemicals, but unless they are pigment loaded they do not provide high reflectivity.

TABLE 3

NICKEL-TIN PLATING BATH		
1.	Sodium Stannate ($Na_2SnO_3 . 3H_2O$)	26.7 grams
2.	Water (H_2O)	650 ml
3.	Glycerine ($C_3H_8O_3$)	200 ml
4.	Sodium Fluoride (NaF)	8.4 grams
5.	Ammonium Bifluoride ($NH_4F.HF$)	11.4 grams
6.	Nickel Acetate ($Ni\ (C_2H_3O_2)_2 . 4H_2O$)	25 grams

TABLE 3-continued

NICKEL-TIN PLATING BATH		
7.	Ammonium Hydroxide (NH_4OH) 58%	120 ml
8.	Hypophosphorous acid (H_3PO_2) 50%	44 ml
9.	Temperature	65°-70°C.
10.	Plating Time	1 minute

Magnetic Material Attachment

In order to properly perform according to the present invention, two spheres, which have been heat treated and plated in the manner described above, must be attached together with their preferred directions of orientation parallel to provide a particle, as generally indicated at **14**, FIG. **5**. Several procedures have been used for attaching the spheres, including semi-random soldering, and direct joining, either upon an individual two-by two basis or upon a quantity basis. A satisfactory technique of attachment to be described below, has been evolved upon a quantity basis.

Tooling

The photoengraving art can be utilized to provide a metal plate, number **15**, FIG. **2**, which is equivalent to a halftone screen and contains a number of equally spaced and accurately sized dimples, **16**, in each square inch. The plate is prepared by starting with a distortion free negative as a basis for exposing a light sensitive dichromate and gum resist that has been applied to the metal plate surface. By using suitable controls during an etching step, dimples of uniform diameter and depth can be formed without undercutting around the edges. According to the present invention, the dimples were made substantially 4 mils in diameter and 4 mils deep, where 1 mil is understood to be 0.001 inches. These were then reduced in size by applying a layer, **17**, of suitable material by electroless plating techniques, since the deposited material will fill in the sides of the dimple as it elevates the level of the plate surface. Plating three mils of metal thickness was found to reduce the size so that each dimple would hold a single 20–30 micron diameter sphere, **10**, as indicated in phantom lines. In the present instance, a copper photoengraving plate was used, with 6000 dimples per square inch, and the dimples were reduced to size by electroless nickel plating. In the following described procedure, a liquid resin will be applied to the dimpled surface, and when dry the resulting film is stripped from the surface. To minimize adhesion of the resin to the nickel surface, the dimples are plated one-quarter mil oversize and then reduced to size by applying a layer, **18**, of teflon that will cure to one-quarter mil in thickness. The teflon is applied by spraying, and cured at approximately 600°F.

Attachment Using The Tooling

The treated and plated spheres are magnetically erased to remove any residual field, then brushed onto the teflon surface of the plate **15** to place a sphere **10** within each dimple, as shown in FIG. **3**. Any spheres remaining on the surface of the plate are readily removed by means of a known adhesive material such as a conventional adhesive tape. A thin film of a suitable resin solution is next applied to the surface of the plate. Although a number of thermoplastic resins and resin combinations can be used, including vinyls, acryloids, certain commercial paints, and even shellac, it has been found that a mixture of acryloid resins dispersed by ball milling 10 percent by weight of Acryloid A-11 and 90 percent by weight of Acryloid B-72 to make about 35 percent by weight in toluene, provides a film that following drying has good dimensional stability and very satisfactory handling quality for the procedure to be described. Application of the acryloid to the surface of the plate is accomplished by conventional techniques; and a drawdown bar calibrated in mils of applied thickness has been most satisfactory in providing films that dry to thicknesses from one to ten mils.

As soon as the resin is applied, the plate is subjected to a directional magnetic field of a strength in the order of 20 to 150 oersteds. A convenient method resides in the placing of the plate and resin between the unlike poles of the two directionally magnetized materials, such as plastoid magnets, so that the field passes from pole to pole through the spheres and parallel to the surface of the plate. Field strengths in the above range are sufficient to cause the spheres contained in the dimples, and suspended in the resin filling the dimples, to rotate so that the prealigned or preferred direction of orientation of each sphere is aligned parallel to the surface of the plate and parallel to the surface of the thin resin film. The electroless nickel on the plate has sufficient phosphorous content and is sufficiently thin so that it does not divert the magnetic field and prevent free orientation. The resin applied at a thickness of about 5 mils will, upon solvent evaporation in air over a period of 15 to 20 minutes, leave about 2 mils of hard but flexible transparent film which, when stripped from the teflon surface to which it has limited adhesion, will display 6,000 peaks per square inch, each peak containing an Alnico 5 sphere oriented with respect to preferred direction of magnetization. Any residual field in the spheres can be magnetically erased by using a conventional AC magnetic field eraser. Resin films thicker than 2 mils are equally satisfactory, however as the thickness is reduced below 2 mils there is danger of tearing the film during stripping.

For the purposes of this invention, two resin films containing magnetic field oriented spheres are prepared. Spheres in corresponding positions, that is, cast from the same dimple in the plate, are to be registered for attachment so that they must be in identical positions with respect to overall film to film alignment. One means for establishing and maintaining the positioning embodies a direct alignment by mechanical positioning devices such as employed in the registration of color separation negatives in the printing of color motion picture films. Positioning accuracy of 0.2 to 0.4 mil is common practice at motion picture film printing rates. Two sets of metal register pins fitting the perforations of a 70 mm films are accurately mounted at each end of the dimple containing plate so that the perforations of a length of film placed along the plate would fall on the pins. A 2 to 3 inch length of 70 mm film base is attached through two perforation holes to each set of pins. The drawdown layer of resin as previously described above is applied and overlapped onto these two 70 mm films, thus forming a firm bond with the 70 mm plastic base. Using this technique, two identical sphere containing resin films may be prepared and stripped from the plate. For convenience in handling, a width of conventional five ounce per inch paper base adhesive tape can be applied to the exposed surface of the resin

after drying and prior to stripping it from the plate. This is a protective measure, and the tape is easily removed at any time. When the two resin films are assembled by again placing the same perforation holes of the 70 mm film base on the same register pins, the tiny spheres will be exactly superimposed, their preferred directions of orientation will be parallel, and parallel to the surface of each resin. If two identical mirror image dimple plates are used, the films of the suspended spheres will be mirror images of each other. In a practical embodiment of the invention, a single dimple plate was used and the two resin films were handled in such a manner that mirror images were prepared and mirror image spheres could be joined together. This was accomplished by stripping one film from the plate and turning it over to expose the projected dimples containing the spheres. The exposed surface was then coated with about 5 mils of resin solution to cover the dimples and provide a protective layer over the spheres. When dry, the film was turned over to expose the original surface and mild sanding was conducted with a 600 W emery paper or equivalent to abrade this surface and expose a 10–15 micron diameter area of each sphere. when viewed under the microscope, the Alnico 5 center, and the electroless plated metal rings were clearly visible. For mirror image positioning, the second resin film needs only reversal and abrasion of the projected dimples. However, to simplify handling and maintain dimensional stability this film was given a very thin resin overcoating to strengthen it to withstand the abrasive action.

A better understanding of this procedure will be obtained from a consideration of FIG. **4** which shows at (a), a diagrammatic representation of the two resin films **19***a* and **19***b* containing spheres that have been stripped from the dimple containing plate. For simplicity these are labeled top and bottom and although this designation will be followed throughout the description it will be understood that it relates only to the relative position of the two when superimposed for joining. Following along, (b) shows these films with a resin layer **20***a* and **20***b* applied over the spheres in each case, and (c) shows the FIG. **4** (b) films **19***a* and **20***b* with the cross-section of the spheres exposed by sanding **20***a* and abrading away **19***b*.

A step of tinning is indicated at (d), and (e) shows the film just prior to assembly for joining. The projected areas **21** resulting from tinning are visible. It will be noted that the two films ready for sphere cross-section joining are mirror images with respect to the plate upon which they have been prepared. The assembly for joining with heat that fuses the alloy **21** with which the metal surfaces have been tinned, is shown at (f), while the magnetochemical particles **14** prepared by this joining process after the supporting resin films have been completely dissolved, are indicated at (g).

As abraded, the exposed metal surface are level with the resin surface. To elevate them above the resin, the surfaces can be chemically displaced with copper or electroless copper plated after step (c) and prior to step (d). Although this is not an essential operation, a 3 to 4 micron copper layer can be deposited over the exposed metal surfaces to provide a space differential permitting subsequent tinning with minimum deposition of tinning material on the resin.

A number of adhesives are suitable for joining pairs of spheres, and substances like sulfur, vinyl suspensions like Wilhold Glue, cyanoacrylate adhesives like Eastman 910 Cement, acetates like Duco Cement, Epoxy containing cements and Woods metal have been used. Rupture occurs in the frangible copper layer at the magnetic metal surface. The fusible alloys were found most satisfactory. Within the fusible alloy group, one known as Cerrolow 117, melting at about 117°F. and containing Indium, Bismuth, Lead, Tin, and Cadmium, has been found to be very satisfactory. Another known as Cerrolow 105 differing from Cerrolow 117 in the addition of a small amount of mercury has also been found to be satisfactory. The alloys can be used singly or in combination; soldering flux often productive of corrosion is not required. Tinning is accomplished by mounting the resin film around a cylinder to expose the abraded sphere areas and advancing it against a flat surface covered by a thin layer of molten fusible alloy. The surface can be a smooth copper sheet, tinned with the alloy and maintained at 60°C. to 90°C. The friction of the exposed spheres against the molten metal results in tinning, and a thin layer of fusible alloy, **21**, is thus applied to each sphere. The alloy is allowed to cool and solidify and the tinned sphere interfaces are ready for joining. Although tinning of exposed metal surfaces in both top and bottom sphere containing films has been described in connection with FIG. **4**, satisfactory results can be obtained by leaving out the 3 to 4 mil copper layer described hereinabove and tinning only one of these films. A rolling contact against the thin layer of fusible alloy will deposit a tiny droplet of alloy on each exposed metal surface, and flow during the joining step is sufficient to bond both surfaces.

The two resin films are superimposed face to face and aligned on the plate using the same 70 mm perforation holes and register pins used in preparing them. The assembled films can be viewed under high magnification to insure that the spheres are superimposed, then subjected to 60°–80°C. heat from a platen heavy enough to maintain the two films in contact. A thin teflon sheet on the surface of the plate and one between the platen and the top film will prevent sticking. After ten to forty five seconds the platen is removed, a cool platen of equal weight is substituted, and the films are allowed to cool. By this action the fusible alloy layers on adjacent spheres will have melted and joined. Following cooling, the composite film and joined spheres can be removed from the plate, the 70 mm perforated base trimmed away the acryloid resin dissolved in a suitable solvent such as toluene or methylene chloride. When the solvent is decanted, the magnetochemical particles remain.

When followed in time sequence, the above described technique provides a supply of magnetochemical particles. If the sequence is interrupted by time delays, the acryloid resin films can shrink so that sphere to sphere alignment for registration is not readily obtained. Control can be introduced by strengthening the acryloid layer with a hard film of polyvinyl chloride or other suitable backing. Polyvinyl chloride thicknesses of 3 to 7 mils have been found satisfactory and can be applied to the back of the two acryloid surfaces after preparation and before removal from the 70 mm register pins. A thin draw-down layer of viscous acryloid can be applied to one surface of the poly vinyl chloride to provide an adhesive of like character for joining onto the dry acryloid layer holding the metal spheres. The poly vinyl chloride, like other suitable plastic strengtheners, will dissolve in the solvents, such as toluene or methylene chloride, or mixture thereof during the re-

lease of the particles as described above.

As a precautionary measure to prevent color forming chemical penetration into any magnetochemical particles not completely sealed by the tinning and joining process or ruptured by rough handling during preparation, a post sealing treatment can be applied. A very thin film of nickel-tin deposited from an electroless plating bath will provide additional sealing against penetration of chemicals as well as provide a surface readily wet by the viscous water phase mixture. The film can best be applied over the several metal exposures by normalizing the surfaces with a thin copper flash followed by the nickel-tin plating. Although a number of combinations have been used, the following procedure has been found effective in depositing a sub micron thickness film providing sealing without appreciably increasing the strength of the sphere to sphere bond. The copper flash can be deposited using the electroless copper bath set forth in Table 2. The formaldehyde (CH_2O) is omitted and plating is conducted at 40°–45°C. for about 10 minutes. The bath is poured off, the particles rinsed with water, then treated for about 5 minutes with a 0.1 percent solution of sodium borohydride ($NaBH_4$). This solution is decanted and the particles are nickel-tin electroless plated as set forth in Table 3. Following plating, they can be rinsed and added to the water phase mixture.

The Magnetochemical Particle

Each particle consists of two spheres joined together by about 2 microns of fusible alloy **21** as shown in FIG. **5** such that satisfactory resistance to the color forming chemicals is provided. By preparation in this manner, the direction of orientation of the adjacent magnetic spheres is parallel. When subjected to a magnetic field, the magnetostrictive forces produce a dimensional change tending to weaken or destroy the bond between the iron and copper layers **11** and **12**, respectively. Magnetic induction establishes like poles in adjacent areas of the spheres as shown by the phantom lines **15'** and **15''**, and these have sufficient force of repulsion to rupture the protective film and allow the spheres to peel apart. Since a hard magnetic material has been used, two permanent magnets have been generated and a force of repulsion exists following the triggering pulse. The measured rupture strengths of the several metals involved at the sphere to sphere interface show that the weakest bond is between the fusible alloy and the Alnico 5. Thus, peel-off occurs at the smallest of the two interfaces resulting from joining, and between the alloy and the magnetic material. This exposes the thin ring of iron to the color forming chemicals contained in the surrounding environment as described in U.S. Pat. No. 3,281,669 and a visible change occurs immediately. Instant separation is available with magnetic fields as low as 100 oersteds and pulse times as short as 2 microseconds (the limiting time on available measuring equipment).

Packaging of the Magnetochemical Particle

It has been found desirable to modify the technique described in U.S. Pat. No. 3,281,669 to more effectively package the above described somewhat more massive magnetochemical particle. The modifications include changes in the composition of the water phase components making up the surrounding chemical environment to permit formation and suspension of slightly larger droplets in the resin film. The following technique has been found effective. Mix equal parts by volume of glycerine and glucose. Stir and blend together well. To the glycerine-glucose mixture add an equal volume of water and blend thoroughly. To 100 ml of this solution add 2 grams of boric acid (H_3BO_3) and 0.5 grams of 2,2' dipyridine. The magnetochemical particles are readily wet by this water phase solution and can be added to it. A dispersion of particle containing droplets in an acrylic resin is made by stirring one part of the above prepared water phase solution containing the magnetochemical particles with three parts of an acryloid solution comprising 40 percent acryloid resin solids in a suitable solvent such as toluene, methylene chloride, or a mixture thereof. The extent of stirring determines the size of the particle containing droplets that are formed, and with particles made using the 20–30 micron diameter spheres described hereinabove, a few moments of mild stirring will provide a very uniform dispersion of water phase droplets averaging about 60 to 80 microns in diameter, each containing a mobile magnetochemical particle. For smaller particles made by joining smaller ferromagnetic spheres, smaller droplets are desirable since the resolution of a pattern will be greater and the total thickness of the final resin film can be decreased. Smaller droplets are readily formed by reducing the viscosity of the water phase or by prolonging the stirring or increasing the stirring rate or both. The resin solution can be applied to a variety of surfaces by conventional coating techniques such as rollers, drawdown, knife edge and the like and the film will dry rapidly by solvent evaporation. A protective resin topcoat can be applied to incorporate desired surface characteristics.

Use of Magnetochemical Particles

Since the product is magnetic field sensitive, writing, printing, or recording can be conducted by any technique that provides a directional magnetic field of the proper strength and with the desired resolution. For optimum high speed high resolution performance, it is desirable to prealign the magnetochemical particles in the water phase droplets by subjecting the resin film to a magnetic field parallel to the intended direction of the field to be used for recording or printing. The field strength should not exceed 50–60 oersteds and could well be an alignment step just prior to use. The conventional magnetic recording head provides the most common source of recording. By selection of gap shape and size, patterns can be constructed of points, lines, or areas. Line structure can be tight since the fringe flux from the sides of the magnetic recording head does not erase a previously recorded pattern to limit packing density as it does during magnetic tape recording. A "bit" at a time printing results from using a rotating metal helix sweeping over a magnetizable bar with the recording material in between the helix and the bar. If the bar is made the core of an electromagnet, then when the bar is pulsed the metal of the helix will concentrate the magnetic field and cause printing at the intersection of the bar and the helix. One rotation of the helix will print a line of "bits." As a refinement, the helix can consist of a sequence of points to effect character generation as described in U.S. Pat. No. 3,017,234 covering Electromagnetic Printer. Magnetizable type can be used for printing in several ways. If the type is pre-magnetized, a print is made upon or just short of contact. If several sheets of the recording material rest on a magnetic metal plate, stack printing will

occur. If the type is the core of a solenoid, an electrical pulse will effect printing. A directional magnetic field can be established at a level just below that necessary to record so that bringing the metal type into recording position will concentrate the magnetic field and cause printing. An area printing source results from the use of a recording on a magnetic tape or on a magnetic metal drum. Printing techniques devoid of mechanical motion include an x, y, matrix of tiny solenoids, where printing occurs on point to point basis through programmed electrical signals. It is also possible to use an electron beam by converting the beam energy to magnetic field energy using the chromium manganese antimonides discussed below and printing on the paper placed against a special CRT face plate. By use of the antimonides, laser beam energy can be converted into magnetic field energy for printing.

While this invention may be applied in the many ways described in the referenced U.S. Pat. Nos. 3,281,669 and 3,512,169, the capabilities of magnetochemical particle performance at low magnetic field levels greatly broadens the scope of application. For example, a color copying device may consist of a television camera reading station using a rotating color wheel so arranged that three primary color aspects of an original are obtained and transmitted sequentially as electrical signals. The signals thus generated may be used to trigger current flow into an *x*, *y* matrix writing station of tiny solenoids to form magnetic fields in each solenoid at the matrix surface. With a magnetic field bias applied to the solenoids, mild excursions of current will effect writing on a point-to-point basis upon a film or paper, embodying the invention and placed against the matrix surface. As a further example, a transformation from an optical image to a magnetic field productive of visual patterns through magnetochemical action is available by utilizing the thermal properties of the chromium manganese antimonide alloys. These materials undergo a transition from antiferromagnetic to ferrimagnetic at a temperature dependent upon alloy composition. The thermal differential resulting from projecting an optical image upon a thin sheet or mosaic of small particles of the alloy will cause this transition. Concentration of magnetic flux in the ferrimagnetic areas will effect magnetochemical action in a paper embodying the invention and placed against the unexposed surface of the alloy and between the alloy and the bias magnetic flux sources to be concentrated. If the alloy is sandwiched between two hard magnetic materials having prealigned or preferred directions of orientation aligned parallel to the longest direction of the composition, then the increase in permeability of the alloy, following the thermally induced transition will result in a magnet of length equal to the composite length, and the extension of field from this longer magnet will effect magnetochemical action.

MODIFICATIONS AND COMBINATIONS

The heretofore mentioned patents relate to magnetochemical particles where performance is based upon magnetostrictive action. This present invention describes a magnetochemical particle wherein the forces generated through magnetostriction and the forces generated through induction of like magnetic poles in adjacent metals or metal alloys combine to bring about a triggering action for color formation not available through either force alone. Similarly, the invention includes a magnetochemical particle capable of triggering a chemical reaction when subjected to a magnetic field wherein the forces of magnetostriction may be small in comparison with the forces generated by like magnetic poles such as, for example, but not limited to, the best permanent magnetic materials. Conversely, the invention also includes particles wherein the forces of magnetostriction are large in comparison with the forces generated by like magnetic poles such as for example, but not limited to, ferrite materials. Performance within this scope is available with a variety of combinations.

For magnetochemical particles of the same composition but different sizes, the induced forces of repulsion vary with the spherical radius so that different size particles will respond at different applied field strengths. For example, 60 micron diameter spheres will respond by rupturing a 20 micron diameter interface at the 100 oersted level, and 10 micron diameter sphere will respond by rupturing a 5 micron diameter interface at the 1000 oersted level. The spheres making up the magnetochemical particle may be of different magnetic materials. For example, a highly magnetostrictive material combined with one of lower magnetostriction can result in a preferred cross section of rupture. Thus, there are many combinations of materials and physical properties permitting the formation of magnetochemical particles falling within the scope of this invention. Although iron has been selected as the preferred color forming metal, very good results have been obtained with electroless deposits or displacement films of metals such as cobalt, nickel, zinc, cadmium, lead, vanadium, silver, copper and tin. Thus, the magnetochemical particles described herein have a variety of parameters that can determine performance and are applicable to selective triggering to form a multi-colored system as described in U.S. Pat. No. 3,512,169. Particles made from spheres have been described throughout this invention, but it will be understood that plates, rods, and other shapes are equally applicable according to the invention.

Although the descriptive techniques have covered the use of magnetic material and metal films plated onto the magnetic material as components for color forming purposes, it will be understood that color forming components can be introduced by other means. The several sphere to sphere bonding materials discussed hereinabove are equally applicable, if each contains a small quantity of metal powder or water soluble or insoluble salts dispersed therein. This does not alter the adhesive character, bond strength, or ease of handling and has the advantage that rupture of a sphere to sphere junction made up of such a loaded adhesive or alloy will expose enough of the loading material to bring about dissolving and color formation. Sulfur, for example, has been loaded with cobalt chloride salt such that upon particle rupture the soluble cobalt salt is immediately dissolved to react with a nitroso R indicator in the surrounding environment to generate a red color. The fusible alloys have been loaded with iron, cobalt, and the like metal powders that are sealed over during the above described joining process, but are exposed to chemical action in the surrounding environment by magnetic field induced rupture. Similar results have been obtained by incorporating small quantities of water soluble salts such as ferrous sulfate into the fusible alloys. Upon rupture, they are immediately available for color formation.

Throughout the description, emphasis has been placed upon the capability of forming a visual pattern in a clear film by application of a magnetic field. It will be realized that the invention is equally applicable to forming a visual differential in whole or in part by bleaching an existing pattern or changing the color of an existing area. Exposure of a number of dyes and pigments to the reducing activity of zinc metal in a slightly acid medium will result in decolorization. The formation of colorless leuco bodies by dyes of the triphenylmethane class such as, malachite green and the reduction of prussian blue pigment to ferrous ferrocyanide are examples. The complexing activity of soluble sulfites on dyes of the fuchsine class, for example, will cause immediate bleaching of color in a water phase droplet containing the colored substance.

The described techniques have covered the use of the magnetochemical particle to generate a visible change in a water system and on a small droplet basis. It will be understood, however, that the invention is equally applicable to situations involving large liquid volumes. It is also equally applicable to organic solvent systems where it may be employed upon a small droplet or large liquid volume basis. For example, the magnetochemical particle actuated by a magnetic field can expose appropriate metal surfaces, salts, or traces of compounds sufficient to catalyze changes in organic based systems and by employing the techniques and controls discussed hereinabove, the changes can be made selective for more than one release. Although packaging has been described in terms of a suspension of water phase droplets, it will be understood that conventional encapsulation techniques are applicable to contain the particle and a suitable chemical environment in permeable, semi-permeable or non-permeable shells to permit handling in solid form.

While it is realized that the invention is applicable to pressure sensitive pattern formation, and this has been demonstrated by suspending the water phase droplets in a resin that has been plasticized with conventional substances like castor oil, di butyl phthalate, or tri cresyl phosphate, for the intended purpose of the invention, this has been avoided. A moderately hard resin has been employed so that cutting in shear would not result in breaking particles and forming color at the sheared edges of a product.

From the foregoing description, the uses, advantages, and operation of the present invention will be readily understood by those skilled in the art to which the invention appertains. While certain forms of the invention have been described, which are now considered to be the best embodiments thereof, it is to be understood that the forms shown are merely illustrative and that the invention is not to be limited to the details disclosed herein, but is to be accorded the full scope of the appended claims.

We claim:

1. A supporting medium having a coating containing high sensitivity magnetochemical particles comprising two anisotropic masses of magnetic material and means capable of chemical activation in response to an applied magnetic field to provide a visible pattern in the area exposed to such magnetic field.

2. A supporting medium having a coating, comprising: a plurality of distinctly chemically different high sensitivity magnetochemical particles comprising two anisotropic masses of magnetic material and including materials adapted to react with a chemical environment within which the particles are contained to provide distinct visible colors, each of said particles being capable upon exposure to a magnetic field to form a visible color of a multicolor image, and said chemical reactions to form distinctly different colors being selectively activated by predetermined characteristics of said magnetic field.

3. A supporting medium according to claim **2**, wherein the color gradations for each color are determined by the intensity of the magnetic field.

4. A supporting medium according to claim **2**, wherein the image characteristics are dependent upon the magnetic field strength and its duration.

5. A supporting medium according to claim **2**, wherein the multicolor image is formed in real time.

6. Magnetic field responsive means, comprising:

a. a carrier medium;

b. small water phase droplets in said medium, each containing a color forming chemical;

c. at least one high sensitivity magnetochemical particle confined in the chemical of the droplet, said particle comprising: a pair of attached masses of ferromagnetic materials having their maximum anisotropic axes parallel;

d. each of said masses being coated with a metal which is reactive to the droplet chemical; and

e. an overcoating of a protective material normally shielding the reactive metal coating with respect to the droplet chemical.

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