May 12, 1970 L. S. TRIMBLE 3,512,169

MAGNETOCHEMICAL METHOD AND MEANS FOR CREATING VISIBLE DISPLAYS IN COLOR

Filed Oct. 20, 1965

4 Sheets-Sheet 1

FIG. 1.

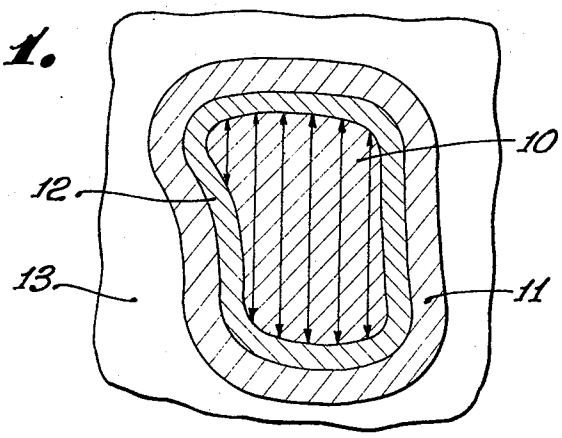
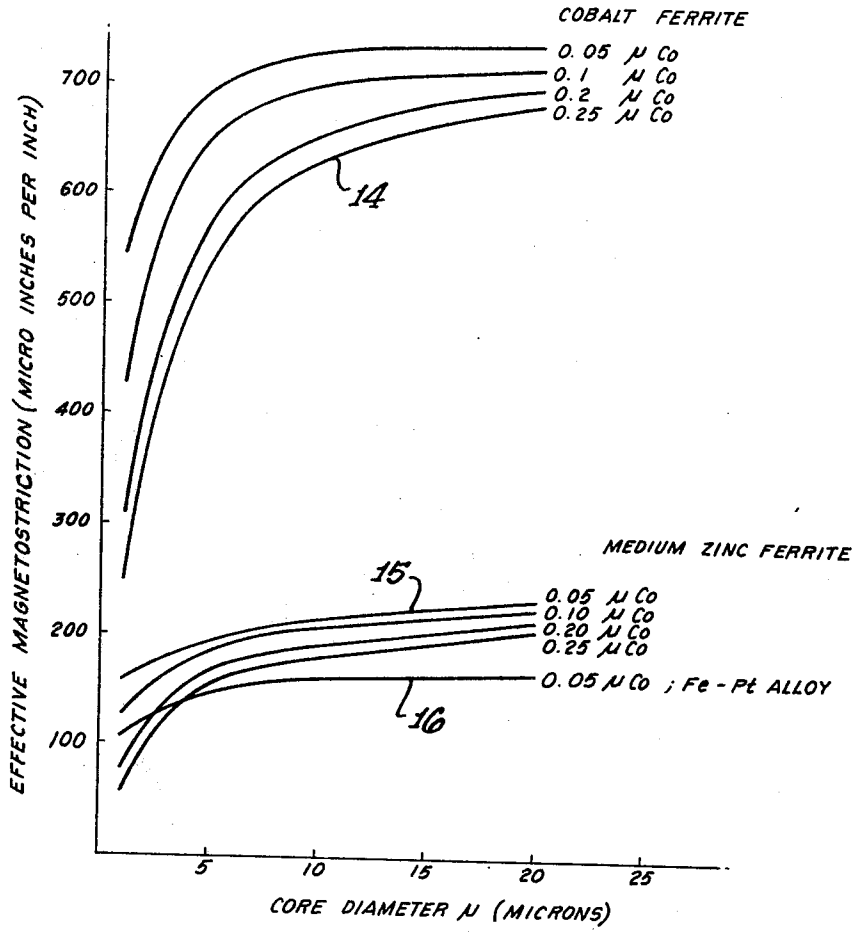


FIG. 2.



INVENTOR.
LYNE S. TRIMBLE
By Robert W. McMorgal
ATTORNEY.

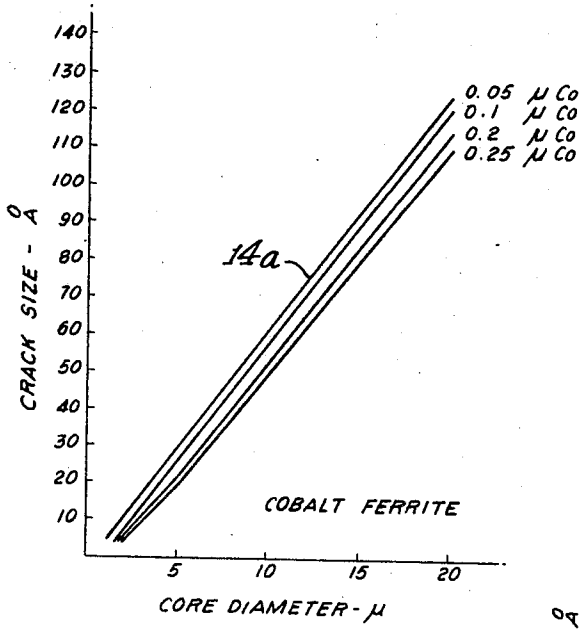


FIG. 3a

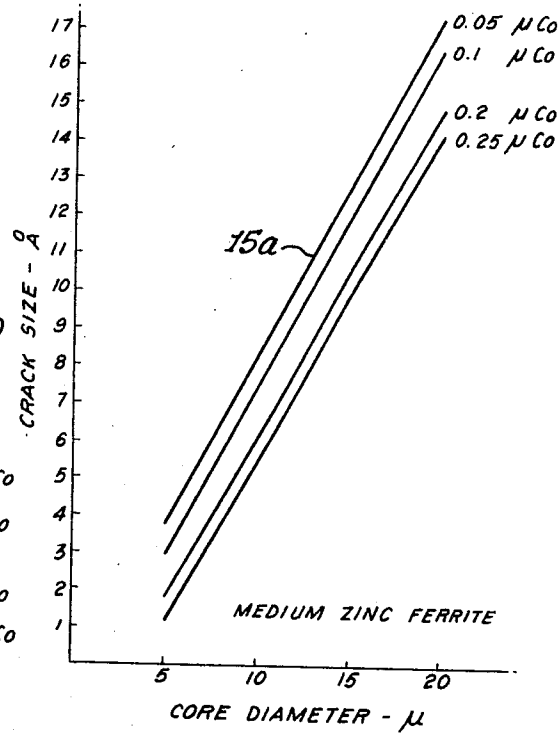


FIG. 3b

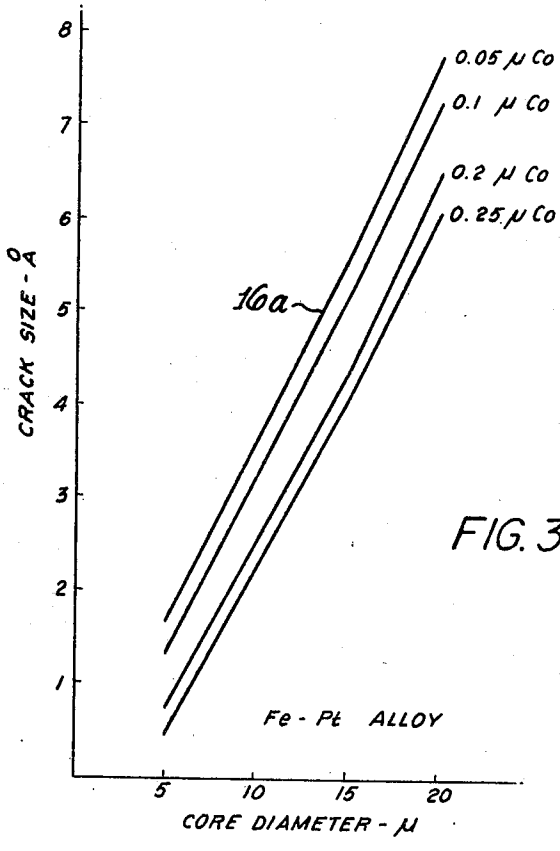


FIG. 3c

INVENTOR.
LYNE S. TRIMBLE
By Robert M. McMorrow
ATTORNEY.

May 12, 1970 L. S. TRIMBLE 3,512,169

MAGNETOCHEMICAL METHOD AND MEANS FOR CREATING VISIBLE DISPLAYS IN COLOR

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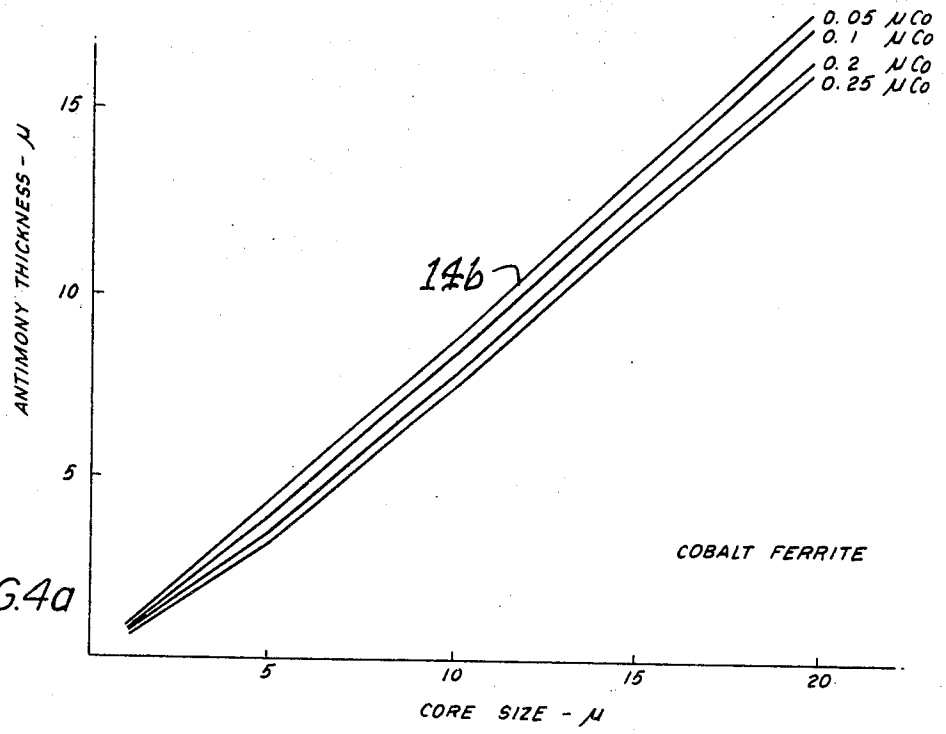


FIG. 4a

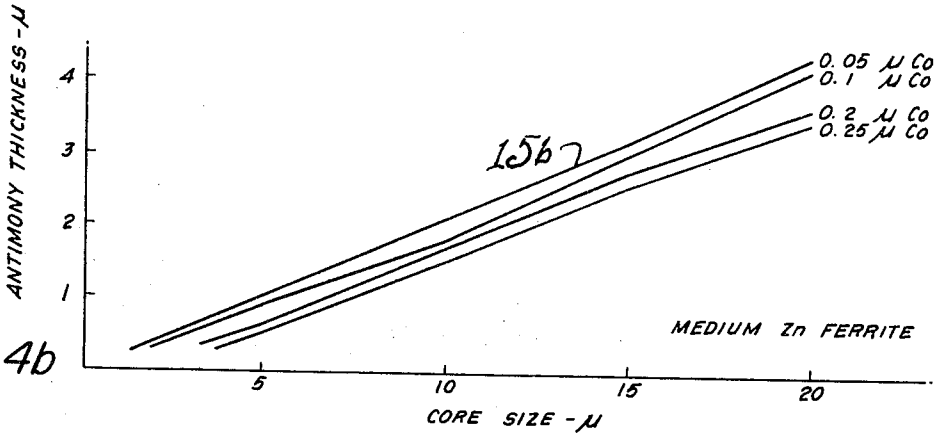


FIG. 4b

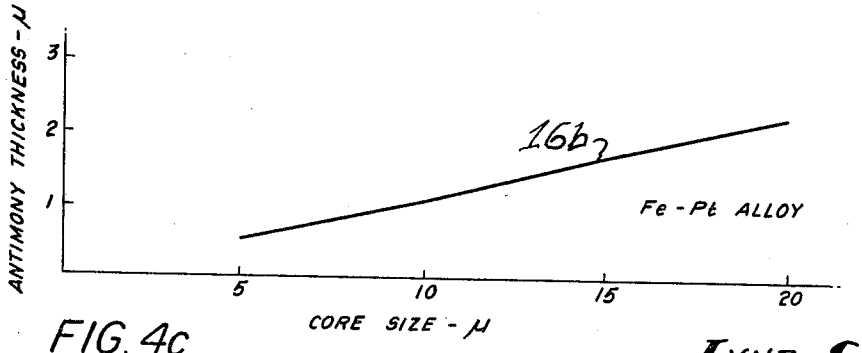


FIG. 4c

INVENTOR.
LYNE S. TRIMBLE
By Robert M. McKenna
ATTORNEY.

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MAGNETOCHEMICAL METHOD AND MEANS FOR CREATING VISIBLE DISPLAYS IN COLOR

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FIG. 5.

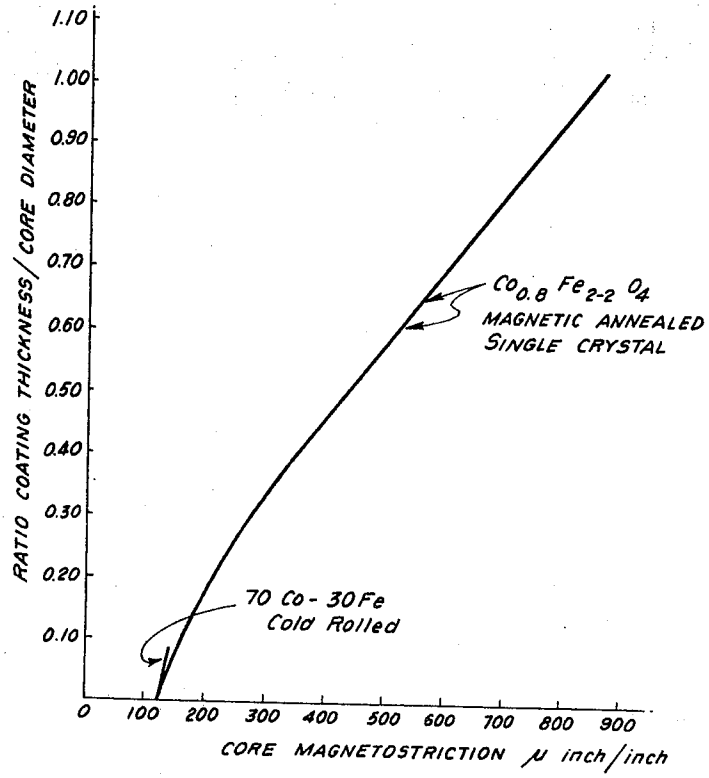


FIG. 6.

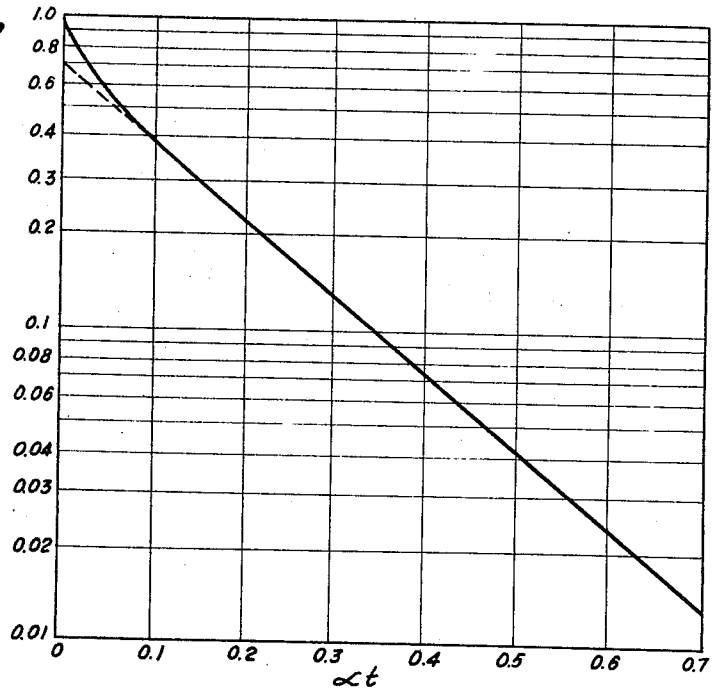
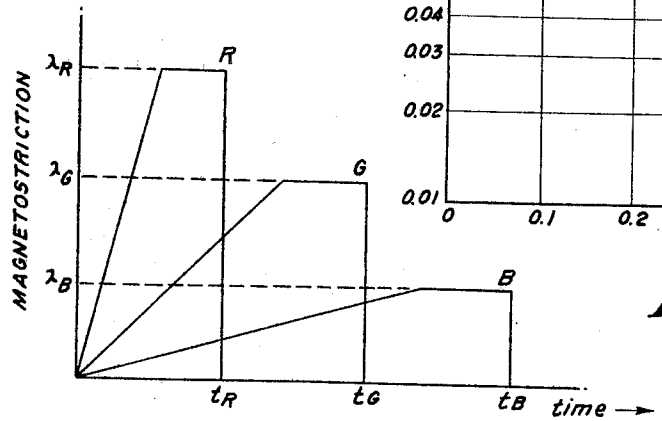


FIG. 7.



INVENTOR.
LYNE S. TRIMBLE
By Robert M. McManigal
ATTORNEY.

United States Patent Office 3,512,169
Patented May 12, 1970

3,512,169

MAGNETOCHEMICAL METHOD AND MEANS FOR CREATING VISIBLE DISPLAYS IN COLOR

Lyne S. Trimble, 4724 Arcola Ave., North Hollywood, Calif. 91602

Filed Oct. 20, 1965, Ser. No. 498,986
Int. Cl. G03g 19/00; G01d 15/34
U.S. Cl. 346—74 22 Claims

ABSTRACT OF THE DISCLOSURE

Method and means for the controlled production of a plurality of primary colors in a single film, wherein normally colorless magnetochemical particles, each of the particles comprising a magnetostrictive core, a brittle coating and a core overcoating in the form of an interlayer of metal, are surrounded with a proper chemical environment which will react upon particle rupture with the interlayer metal of the core to produce a primary color. Color activation is accomplished by a triggering reaction which ruptures the particles when subjected to properly chosen magnetic pulses, the core, coating and interlayer having selectable control parameters influencing the triggering of the reaction, and which permit selectivity as to the respective color producing particles.

The present invention relates generally to the method of and means for creating visible patterns in different colors, and is more particularly concerned with method and means which respond to magnetic field stimulation at micro-second rates.

The requirement to present information for visual display at very rapid rates has been developed by the wide spread use of high speed electronic equipment and in particular the demands for rapid presentation of information received from satellites. In the latter case, the information is often presented by enlarged projection to screens under high illumination levels, so that viewing is possible under ambient lighting Monochrome information display has been satisfactory. Current demands include the recording and display of information in several colors.

In formation can be recorded and presented at real time rates by techniques associated with monochrome television. The state-of-the-art has advanced to the point where rapid photographic, thermoplastic, photochromic, electrostatic, and other techniques can provide a permanent visible record in real time. There is a need for a real time presentation method to display and rapidly update various colors. The techniques associated with color television have not been suitable for providing a record that can serve for real time viewing and storage without involving substantial post treatment.

The approaches to solving this problem and providing a color display in real time capable of rapid updating, have not been satisfactory. One has been to utilize direct recording upon existing photographic color reproduction processes and attempt to minimize the time between exposure and projection for viewing. Although the wet processing time has been reduced from about 55 minutes

to 3 or 4 minutes, further reduction is limited by the many chemical steps required to provide the multi-color image. Improvements have resulted in color reversal packs that will provide a color print in one minute. A second approach to providing color in real time embraces a host of systems based upon primary color separation methods. The best rapid monochrome techniques have been utilized in triplicate with primary color filters to record the color aspects of the subject. Upon reproduction, color filters are again required and the three images must be superimposed or registered in presentation for real time viewing.

A fundamental approach to providing a visual display by an entirely different technique has been described in the copending application of Lyne S. Trimble, Ser. No. 269,993, now Pat. No. 3,281,669, entitled Means and Method for Indicating and Visibly Permanently Recording a Magnetic Field. In that application a chemical reaction is triggered by means of a magnetic pulse. Since the chemical reaction is spontaneous, a substantial visible change can result from a magnetic pulse that is microseconds in duration. In contrast with the copending application, the present invention relates to selectively triggering spontaneous chemical reactions so that the production of three primary hues in a single film layer is possible.

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

(a) 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.

(b) The provision of method and means whereby the application of magnetic pulses of different characteristics will generate at least two primary colors for visual display purposes.

(c) The provision of method and means whereby the application of magnetic pulses of different characteristics will generate visible color effects upon a real time basis.

(d) The provision of method and means whereby combinations of suitable quantities of the primary colors to be viewed as an area will create secondary colors.

(e) The provision of an additive three color film, wherein the colors are stimulated by magnetic means.

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

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

FIG. 1 is an enlarged (highly magnified) cross sectional view of a magnetochemical particle as embodied in the present invention;

FIG. 2 is a graph showing the effective magnetostriction for varied core diameters of different materials;

FIGS. 3 (*a*, *b*, and *c*) are graphs showing crack size variations for different core diameters for different materials;

FIGS. 4 ,*a, b* and *c*) are graphs respectively showing the relationship between the maximum brittle coating thickness and core size;

FIG. 5 is a graph indicating the ratio of acceptable coating thickness to core diameter with respect to core magnetostriction;

FIG. 6 is a graph which illustrates magnetic flux build-up as a function of response time; and

FIG. 7 is a graph illustrating magnetostriction field levels with different time responses, the combination permitting selective activation of primary colors.

Referring more specifically to the drawings, the basic concepts of the present invention will be explained primarily with respect to the method and means of obtaining selective action.

As described in the aforementioned Trimble patent, the production of a visible pattern is dependent upon the use of a magnetostrictive material coated with a brittle, chemically resistant substance. When this magnetochemical particle is placed in a chemical color forming environment and exposed to a magnetic field, the change in size of the magnetostrictive core ruptures the brittle coating and allows chemical access to the core. The result of this access is a spontaneous chemical reaction productive of a voluminous colored product.

Referring to FIG. 1, there is shown a cross sectional view of a magnetochmecial particle according to the present invention, such particle having a magnetostrictive core **10**, a brittle coating **11**, and an interlayer of metal **12**, all of these providing control parameters which have an influencing affect upon the triggering of the reaction by selective magnetic field action.

The particle just described is surrounded with a proper chemical environment, as indicated at **13**, which is chosen to react with the interlayer metal (or magnetostrictive core) in response to a triggering action which can be controlled as a function of the elongation of the core in a magnetic field. The parameters include particle size and change in size $(\Delta l)/l$ for a given magnetic stimulation (H), rupture elongation and thickness of the brittle chemically resistant coating, and thickness of the interlayer.

The particles with chemical environment as described above may be applied as fluid droplets in the form of a coating to a surface of a supporting medium such as a tape of suitable material, film, paper, plastic, and the like. A number of materials may be used for obtaining the objectives of the present invention, and a number of those which have proved successful may be mentioned. The materials of the core **10** may comprise any one of the chemical elements known to be magnetostrictive such as iron, cobalt, nickel, and certain rare earth elements such as gadolinium. The material of the core **10** may also comprise metal alloys like cobalt iron or iron platinum. In addition the materials of core **10** may comprise members of a class known as ferrites described in the aforementioned Trimble patent. Of particular value in connection with this invention are the cobalt ferrites and zinc ferrites. Finally, the materials of core **10** may comprise any of the above listed substances singly or in combination. For the interlayer substance the elements cobalt, nickel, copper, and iron have been used. Other substances capable of being formed as a coating on a magnetostrictive material and having the characteristic of providing a color with a selected chemical environment can be used. For the chemical environment a great variety of color forming substances normally associated with qualitative chemical analysis can be employed. For example, with a cobalt, interlayer, Nitroso-R Salt has been found to provide a brillant red color. With an iron interlayer the Nitroso-R Salt will provide a green color. Blue can be formed by utilizing an iron interlayer with Tiron.

PARAMETER INFLUENCE ON SELECTIVE CONTROL

Although there are a number of parameters that could influence the selective control of the magnetochemical activity in the particle, the primary variables have been found to be:

(1) The extent of magnetostriction exhibited as a change in physical size (which may be either positive or negative), is described as fractional change in length and expressed as micro-inches per inch.

(2) Magnetic field strength causing the magnetostrictive change in size. This field strength directly influences the fractional changes in length of the several magnetostrictive materials.

(3) Thickness and brittleness of the protective coating as properties influencing the conditions under which combinations of (1) and (2) will result in brittle coating rupture. Thickness control can be utilized to separate the responses of uniform size magnetostrictive particles or, variations in thickness between size ranges can be used to equate particle response. In this manner, control of thickness for a given brittle substance can provide two means of influencing the triggering of a chemical reaction.

(4) The inherent period of induction after magnetic field application and before magnetization. This is utilized by controlling the duration of the applied magnetic field strength. Certain magnetostrictive materials, although producing a substantial fractional change in length under the influence of a magnetic field, require an interval of time before a change in length is evident. Others appear to respond so fast that a time interval has not been measured. The selection of magnetostrictive materials of different induction times thus provides a means of obtaining selective response for the production of different visual images.

These parameters can function independently in providing control, or they can also function in an interdependent manner. The discovery and utilization of this interdependence forms an important consideration in the present invention.

The relationships between these parameters have been investigated for a variety of magnetostrictive materials, for a variety of brittle coating substances, for a variety of particle sizes, and for a variety of brittle layer crack widths as these may or may not be influenced by a ductile metal interlayer coating applied over the magnetostrictive core material and between this core material and brittle coating. The purpose of a ductile coating is to allow a more successful and more uniform application of a brittle protective substance as well as provide a variety of chemical color forming metals so that a broad choice of hues is available.

The relationships found to exist between the above noted parameters will hereinafter be discussed. From the obtained data, it is possible to select combinations of magnetostrictive materials, physical sizes of these materials, ductile metal and brittle metal coating thickness for application to these materials, as well as magnetic pulse strength and duration combinations to provide a vast array of real time magnetochemical triggering systems.

MECHANISM OF COATING BREAKAGE

The mechanism of coating breakage hinges on the amount of core elongation allowed by the coating. If the elongation of the core and the coating is greater than the breaking point of coating, cracking will occur and allow chemical action. On the other hand, if the coating is too thick, the core cannot overcome the force exerted on it by the coating and will not be able to stretch the coating to the breaking point.

Magnetostrictive elongation may be considered in two aspects. One is that different materials subjected to the

same magnetic field strength will exhibit different fractional changes in length ($\Delta l/l$) and two, the same material under the influence of different magnetic field strengths will exhibit different fractional changes in length. These two aspects will vary depending upon core size as shown by FIG. 2 wherein the effective magnetostriction of the core materials cobalt, ferrite, medium zinc ferrite and iron platinum alloy has been indicated for different core diameters and for several thicknesses of the cobalt interlayer. The interlayer thickness has been indicated by the curves **14**, **15** and **16** respectively for the various core materials. It will be observed that for core diameters under ten microns, variation of the interlayer thickness provides sufficiently large changes in effective magnetostriction to provide a controllable parameter with respect to triggering operations.

Brittle coating rupture provides a crack through which the chemical environment must penetrate in order to actuate the spontaneous chemical reaction. Cracks wider than the threshold crack width with result in a more extensive chemical reaction and a stronger visual pattern. There must be a certain crack width before a reaction can be obtained. Referring to FIGS. 3(*a*, *b* and *c*), the variation in crack size for different core diameters and several thicknesses of interlayer has been shown by the curves **14***a*, **15***a* and **16***a* respectively for the core materials of FIG. 2. Consideration of these graphs indicates that the divergences of crack sizes for different core diameters or the same core diameter and different thicknesses of interlayer provide another controllable determinant which may be utilized in practising the present invention.

field level with fast build-up can be established to provide for example, a red color, an intermediate field level with a slower build-up can provide a green color, and a still lower field level with a longer build-up time can provide a blue color.

If the red color forming core has, for example, a response time t_R, while the green and blue have response times t_G and t_B respectively, then the field levels can be chosen such that the magnetostriction of R is greater than that of G which is in turn greater than that of B, and the protective coating thickness chosen to crack at these respective levels. Thus, one color can be independently triggered by a magnetic pulse exposing all three magnetochemical centers without affecting the other two. For example, when the green core is triggered, the applied field is too low to break the coating on the red core and the pulse length too short to trigger the blue core. This approach is satisfactorily workable within the limits of the properties of the selected magnetostrictive materials as stated herein, and within the particle size range and metal coating thickness ranges achieved in practice.

In one form of the present invention, it has been desirable to stimulate the formation of three primary hues within a period of eight micro-seconds to result in visible color formation within three seconds at a resolution approaching 1,000 television lines per inch. Under these conditions, a single frame containing 750,000 elements could be recorded and projected for viewing within less than five seconds. To accomplish this the following information has been selected from the figures and graphs discussed above.

	Field level, Oersted	Pulse length, μ sec.	Core diameter, μ	Interlayer thickness, μ	Antimony brittle coating thickness, μ
Red	3,500	1	0.5	0.1	0.2
Green	3,000	2.5	1.5	0.1	0.3
Blue-Violet	2,500	4	2	0.1	0.3

Another controllable parameter resides in the thickness which is used for the brittle coating when considered in connection with different magnetostrictive materials. As an example of this variable, there is shown in FIGS. 4 (*a*, *b* and *c*) by the curves **14***b*, **15***b* and **16***b* respectively, the relationship between the brittle coating thickness of antimony with respect to core size for the same core materials as considered above, for different thicknesses of cobalt interlayer.

FIG. 5 shows the ratio of brittle coating thickness to core diameter as a function of core magnetostriction.

SELECTIVE STIMULATION OF COLOR

The magnetostrictive change in size is generally attributed to magnetic field sponsored domain orientation in the material. The speed of this orientation is, in general, very fast and dependent upon the rate of increase of the magnetic field inside the material, which is in turn controlled by the induced eddy current. The time response of magnetostriction can be estimated by the build-up of the magnetic flux. Based upon a chosen particle shape, size, permeability, volume resistivity, and magnetostriction the graph in FIG. 6 shows the magnetic flux build-up in a particle as a function of response time to an applied magnetic field. Thus, particles can be selected according to their size, resistivity or permeability so that their response times will be different.

As part of the present invention a recording technique has been used based upon the foregoing to make use of the time required with respect to certain materials to build up to a desired field level and obtain a specified magnetostrictive action. Selective activity is available by proper choice of parameters, as shown in FIG. 7. A high

Although the phenomenon of magnetostriction has been covered in its most common occurrence as a fractional increase in length, modification in preparation and annealing technique can provide particles exhibiting a fractional decrease in length under the influences of a magnetic field. For the purposes of this invention either an increase in length or a decrease in length can be employed to trigger a spontaneous chemical reaction.

Various modifications may suggest themselves to those skilled in the art without departing from the sprit of my invention, and hence, I do not wish to be restricted to the specific forms shown or uses mentioned, except to the extent indicated in the appended claims.

I claim:

1. The method of creating visible multicolor patterns and displays, which comprises the steps of:

(a) coating magnetostrictive particles respectively with a ductile metal;

(b) overcoating the ductile metal coating with a chemically resistant coating;

(c) suspending such coated particles in a chemical environment capable of reacting with the ductile metal coatings to form predetermined colors, but normally rendered inactive by said overcoating; and

(d) selectively stimulating color forming reactions by subjecting the magnetostrictive particles to magnetic field pulses.

2. The method according to claim **1**, wherein the magnetostrictive particles are magnetized to reach different flux levels in different intervals of time.

3. The method according to claim **1**, wherein the overcoatings for the color forming particles for each color are of a predetermined thickness, chosen to provide selective magnetostrictive response.

4. The method according to claim 1, wherein the magnetostrictive particles are of a predetermined size for each color.

5. The method according to claim 1, wherein the magnetostrictive particles are of a predetermined material for each color.

6. The method according to claim 1, wherein a plurality of chemical environments are utilized.

7. The method according to claim 1, wherein the coating of the magnetostrictive particles comprises a metal of the class cobalt, nickel and iron, and the overcoating comprises a metal of the class antimony, tellurium, and selenium.

8. The method according to claim 1, wherein the ductile metal coatings are of different materials.

9. The method according to claim 8, wherein the coatings are of predetermined thickness for each color.

10. The method according to claim 1, wherein the overcoatings are of different material.

11. The method according to claim 10, wherein the overcoatings are of different thickness for each color.

12. The method of obtaining multicolor visible patterns and displays, which comprises the steps of:

(a) confining magnetochemical particles within fluid droplets of a chemical environment capable of reacting with the particles therein to produce distinctive colors, said magnetochemical particles having a magnetically rupturable coating thereon; and

(b) simultaneously exposing a plurality of these particles to a magnetic field of particular parameters to selectively rupture the coating on certain of said particles, to cause these particles to chemically react with said environment and form visually different colors in the presence of non-activated particles.

13. A magnetochemical particle, comprising:

(a) an inner core of relatively chemically inert magnetostrictive material;

(b) an outer coating of brittle material that can be ruptured magnetostrictive action and is inert to a chosen chemical environment; and

(c) a substance adapted to react with the chemical environment and provide a visible color, said substance being normally shielded from the chemical environment by said outer coating.

14. A magnetochemical particle according to claim 13 wherein the substance is a ductile metal.

15. A magnetochemical particle according to claim 13, wherein the magnetostrictive effect of the core material and the material of the coating and its thickness are so correlated as to cause coating rupture at a predetermined magnetic flux level.

16. A magnetochemical particle according to claim 15, wherein the magnetic flux level is established in a predetermined response time.

17. A magnetochemical particle according to claim 13, wherein the reaction produces a visible color in a time interval of the order of microseconds.

18. A magnetochemical particle, comprising:

(a) an inner core of magnetostrictive material;

(b) a coating of brittle material that can be ruptured by magnetostrictive action and is inert to a chosen chemical environment; and

(c) a substance adapted to react with the chemical environment and immediately provide a visible color, said substance being normally shielded from the chemical environment by said coating and comprising an interlayer between the inner core and the coating.

19. A supporting medium having a coating comprising a plurality of distinctly chemically different magnetochemical particles including materials adapted to react with a chemical environment to provide distinct visible colors, said particles being in the chemical environment, each of said particles upon exposure to a magnetic field forming a visible color of a multicolor image, and wherein said chemical reactions to form distinctly different colors are selectively activated by predetermined characteristics of said magnetic field.

20. A supporting medium according to claim 19 wherein the color gradations for each color are selectively controlled by the intensity of the applied magnetic fields.

21. A supporting medium according to claim 19 wherein the image characteristics are dependent upon the magnetic field strength and its duration.

22. A supporting medium according to claim 19 wherein the multicolor image is formed in real time.

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BERNARD KONICK, Primary Examiner

J. F. BREIMAYER, Assistant Examiner

U.S. Cl. X.R.

117—36.7; 346—1, 135

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,512,169 Dated May 12, 1970

Inventor(s) LYNE S. TRIMBLE

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 7, line 39, "by" should be inserted after "ruptured".

SIGNED AND
SEALED
SEP 8 - 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents