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(54) **Radiation imagable compositions.**

(57) A radiation imagable composition in which an image can be produced upon exposure to intense radiation is disclosed which comprises (a) at least one component selected from the group consisting of clay and barium sulfate, and (b) a binder material which will not be destroyed during exposure of the composition to intense radiation and will not mask the image produced upon exposure to intense radiation.

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TITLE OF THE INVENTION:

RADIATION IMAGABLE COMPOSITIONS

BACKGROUND OF THE INVENTION:

Field of the Invention

This invention relates to a composition upon which an image can be produced by subjecting the surface thereof to a source of intense radiation, and to the process for producing an image thereon.

Description of the Prior Art

Prior to the present invention, a number of techniques were suggested for producing substrates that could be imaged upon being subjected to a source of intense radiation, such as a laser.

In the majority of the prior art techniques, the substrate is coated with a layer of a composition containing a material that absorbs the radiant energy and becomes vaporized or is otherwise removed from the surface of the substrate. Examples of radiant energy absorbing materials include various dyes and pigments, such as carbon black, and various metals, such as aluminum. If a metallic layer is coated over a dark substrate, for example, selective removal of the metallic layer will produce a positive image. If, however, a dark pigmented layer is coated over a transparent or light substrate, selective removal of the dark layer will result in a negative image.

These techniques have been employed by manufacturers of electronic components in connection with their laser marking systems. Electronic components, such as dual inline packages (DIPs), are first coated with a laser-imagable coating using conventional printing techniques such as silk screen, spraying and offset lithographic. The coated components are then selectively subjected to laser radiation which removes the coating from the areas exposed to produce an image, such as a part number or other form of identification. After printing, the electronic components are cleaned, for example in an HCl bath. Coatings containing metallic particles are attacked by the bath to a sufficient degree to cause severe contamination of the bath and destruction of the coating.

One of the major drawbacks of the laser-imagable coating compositions that have been used is the difficulty associated with matching the color of the coating to the color of the potting compound for the electronic component. Different manufacturers prefer to distinguish their products using different colors. If the laser-imagable coating were metallic, it would have to be coated over a dark colored surface to provide the necessary contrast to the areas in which the coating had been removed by the laser. If, on the other hand, a pigment such as carbon black were to be employed in the coating, there would not be sufficient contrast against the dark background of the potting compound.

Other laser-imagable compositions are prepared with iron oxide yellow as the pigment material. Upon exposure to laser radiation, the areas exposed turn red in color due to the formation of iron oxide red.

What would be most desirable from the standpoint of color contrast, therefore, would be a coating containing a pigment or other material which changed to a color upon exposure to radiation that was in contrast with the original color of the coating. Even if such coatings were developed, however, the original colors would still have to be matched to the color of the substrate. Thus, a number of different colors which matched the colors of the substrates and which also changed to a contrasting color upon exposure to laser radiation would have to be developed.

SUMMARY OF THE INVENTION:

In accordance with the present invention, radiation imagable compositions are prepared in which images are produced when the compositions are subjected to intense radiation. The compositions comprise either a clay or barium sulfate or a mixture thereof in a binder material which will not be destroyed and which will not mask the image produced upon exposure to intense radiation. The binder material can comprise any natural or synthetic resin material or any vitreous or ceramic material.

In a preferred embodiment of the present invention, the composition is essentially transparent or translucent and the image produced upon exposure to radiation is white in color. In this embodiment, the index of refraction of the binder material is greater than that of the clay or barium sulfate.

The compositions of the present invention can be used in a variety of applications, such as coating compositions, molding compounds, potting compounds for encapsulating electronic components or in any other way used to render an article or a surface thereof imagable upon exposure to intense radiation.

In the process of the present invention, an article is made from or coated with the composition of the present invention so that an image can be produced on its surface upon exposure to intense radiation. The areas of the surface of the article on which images are desired are then selectively exposed to an imagewise pattern of high intensity radiation. Lasers have been found to be particularly suitable sources of intense radiation. The surface of the article should be exposed to the radiant energy in an amount and for a time sufficient to produce an image in the area irradiated. A source of radiation having an energy density of from about 0.7 to about 6.0 joules/cm.^{2} has been found to be acceptable.

Because such a variety of compositions can be prepared which contain clay and/or barium sulfate in accordance with the present invention, it has been found that many different articles or surfaces can be rendered imagable or markable with a laser or other source of high intensity radiant energy. This invention significantly increases the versatility of laser marking systems, which are presently limited to the use of a few laser imagable coatings for electronic components.

DESCRIPTION OF THE PREFERRED EMBODIMENTS:

In accordance with the present invention, compositions are prepared in which images can be produced upon exposure to high intensity radiant energy. The compositions comprise either a clay or barium sulfate or a mixture of both in a binder material which is not destroyed during exposure to radiation and which does not mask the image produced upon irradiation of the composition.

The compositions can contain any of the clays and other aluminum silicate-containing materials which occur naturally. Both hydrated and anhydrous aluminum silicate clays can be used. The clay should be added to the compositions of the present invention in finely divided particulate form, such as in the form of thin flat plates. The particle size of the clay has been found not to be important insofar as its ability to function in accordance with the present invention. The smaller the particle size, the more durable to abrasion the coating will be. The coating will also be smoother and more aesthetically pleasing with a smaller particle size.

The amount of clay present in the composition can vary widely. If barium sulfate is present in the composition, no clay need be present. If no barium sulfate is included, however, then the upper limit is simply a function of the surface area of the clay used and the viscosity and rheological properties desired for the composition. The upper limit will be less than the critical pigment volume content (CPVC) of the composition. A critical pigment volume content (or concentration) is defined as that level of pigmentation (PVC value) in a dry coating where just sufficient binder is present to fill the voids between the pigment particles. PVC values are determined as follows:

$$\text{PVC} = \frac{100\rho b}{\rho b + 0.01 \text{OA} \rho p}$$

where PVC = pigment volume content (%),

OA = oil absorption value (pounds of linseed oil per 100 pounds of pigment),

ρb = density of linseed oil binder (0.935 g/cm.^{3}), and

ρp = density of pigment (g/cm.^{3}).

The CPVC of a coating composition represents the densest packing of the pigment particles commensurate with the degree of dispersion of the system. The degree of pigment dispersion exerts a major influence on a CPVC value. A vehicle of high dispersive capacity, such as the linseed oil called for in the oil absorption test, will produce a substantially completely dispersed pigment state yielding a maximum CPVC value. On the other hand, a vehicle of lower dispersive capacity will give a reduced CPVC value in proportion to the flocculation that remains undispersed in the coating composition. See T. Patton, Paint Flow and Pigment Dispersion, Chap. 7, pp. 184-187 (1966). Generally, the compositions will comprise up to about 65 percent by weight, and preferably in the range of from about 15 to about 35 percent by weight, of the clay.

The compositions of the present invention can also contain barium sulfate in lieu of or in addition to the clay. Any barium sulfate or barite can be employed in finely divided particulate form. As is the case with the clay, the particle size of the barium sulfate is only important with respect to the durability and aesthetics of the composition desired. The amount of barium sulfate included in the composition can likewise vary over a large range. If some clay is present in the composition, then no barium sulfate need be included. In the absence of clay, the upper limit on the amount of barium sulfate is governed by the critical pigment volume concentration of the composition. In general, the compositions will comprise up to about 80 percent by weight, and preferably from about 25 to about 50 percent by weight, of barium sulfate.

The compositions of the present invention preferably contain both clay and barium sulfate. It has been observed that when only clay was added, the images produced were not as bright as when both clay and barium sulfate were included, and that when only barium sulfate was added, a higher energy level was required to produce images having the same degree of brightness and clarity as when both clay and barium sulfate were used. Thus, the combination of both materials appears to provide superior image contrast and brightness to that obtained using either material alone. As with either material alone, the upper limit on the amount of clay and barium sulfate in the composition must be below the CPVC. Preferably, the compositions comprise from about 3 to about 35 percent by weight of clay together with from about 15 to about 60 percent by weight of barium sulfate.

The compositions further comprise a binder material for the clay and the barium sulfate. Since the imagable compositions of the present invention can be used in a variety of ways to prepare articles or surfaces of articles that can be imaged by exposure to intense radiation, the composition of the binder is primarily a function of the end use of the imagable composition. If the imagable composition is to be employed as a coating for electronic components, then any conventional coating composition can be used as the binder, provided it exhibits the other characteristics of the binder compositions described herein. Similarly, if the imagable composition is to be used as a potting compound or molding compound, then a conventional potting compound or molding compound can be used as the binder for the clay and barium sulfate.

In order for an image with good contrast to be produced in the composition of the present invention, the binder material should have an index of refraction greater than the index of refraction of the clay or of the barium sulfate. If the index of refraction of the binder is less than that of the clay or of the barium sulfate, then these materials will act as pigments to render the composition opaque upon drying or curing. An image will not be produced upon exposure to intense radiation if the clay and barium sulfate act as pigments for the binder.

It is important that the binder composition not contain any ingredient that will mask the image produced upon exposure to radiation. The principal ingredient used to bind the particles of clay and barium sulfate can be any of the natural or synthetic resins or polymers used to prepare coating, molding, potting or other compositions, such as acrylics, epoxies, phenolics, urea-formaldehydes, polyesters, varnishes, lacquers, shellacs, elastomers, and other resinous materials. It is also possible to employ glass, ceramic or other vitreous materials as the binder. Since the clay and barium sulfate are the ingredients that are common to all of the present compositions, regardless of their particular end use, the binder can be any material that will hold the particles of clay and barium sulfate together sufficiently to form a surface in which an image can be formed. A dye or pigment can be added to the binder composition to produce an article or coating of a desired color, provided that the binder composition in the absence of the dye or pigment has an index of refraction greater than that of the clay or barium sulfate. If the binder composition contains too large an amount of the pigment or dye, however, the image produced upon irradiation of the composition will simply be masked by the color of the pigment or dye, provided that the dye or pigment is not itself destroyed by the radiation.

The binder compositions can also contain any of the conventional additives and modifiers which are generally included in such compositions, such as plasticizers, lubricants, adhesion promoters, flow modifiers, initiators, fungicides, curing agents and the like, depending upon the particular end use of each.

The compositions of the present invention can be employed to provide surfaces upon which images can be produced with high intensity radiant energy. Because many different types of binders can be used to prepare the present compositions, these compositions can be tailored to many widely differing applications. For example, laser marking systems are presently used to produce images on electronic components by subjecting a component coated with a composition containing a laser radiation absorbing material to an imagewise pattern of laser radiation. The coating is removed from the component in the areas subjected to radiation. As discussed above, however, the inability to provide coating compositions that match the colors of the potting compounds for the electronic components and provide sufficient image contrast upon irradiation has severely limited the acceptability of such laser marking systems.

In a preferred embodiment of the present invention, the composition is substantially transparent or translucent and changes color to white upon exposure to intense radiation. Such compositions are prepared by employing a binder material having an index of refraction greater than the index of refraction of either the clay or the barium sulfate. The clay and the barium sulfate in their finely divided form are white in color. Upon mixture of the clay and barium sulfate with a binder material such as a resin having a greater index of refraction, an opalescent material is obtained which cures or dries to a substantially transparent or translucent material. The compositions should not contain any ingredient that would increase the opacity of the composition.

The advantages of such transparent or translucent compositions are manifest. For example, the current problems associated with the use of laser systems for marking electronic components, such as DIPs, are alleviated by such compositions. Since substantially transparent coating compositions can be prepared, there is no longer any need to select dyes or pigments that match the color of the coating to the color of the potting compound of the electronic component and that change color or are destroyed to provide images of sufficient contrast. The white-colored image produced on the transparent coating will provide sufficient contrast against any darker color of the component over which it is coated. Thus, by coating the potting compound that encapsulates the electronic component with a substantially transparent coating that turns white upon exposure to intense radiation, the manufacturer will always maintain the desired color of the potting compound and will obtain sufficient contrast between the image and the background against which it is produced.

As an alternative, the manufacturer of the electronic components could prepare a potting compound containing clay and barium sulfate in accordance with the present invention. By using an essentially standard potting compound as all or part of the binder for the clay and barium sulfate, the manufacturer would entirely eliminate the need for a coating on the electronic components to provide an imagable surface, since the image could then be produced directly on the surface of the potting compound.

Since images are only produced in the areas of a surface having the composition of the present invention which are exposed to the intense radiation, it is immaterial whether the article is entirely made from the present composition or whether it is simply coated with the composition to render its surface imagable. Thus, it can be seen that many articles and surfaces can easily be rendered imagable. If an article is normally made from a composition that contains an inert extender or filler material, then all or part of the extender or filler material can be replaced with clay and barium sulfate in accordance with the present invention to render the surfaces of the article imagable. However, if the article is not usually made from a composition that contains a filler material, then the article can be coated with a coating composition containing clay and barium sulfate in accordance with the present invention to render the coated surfaces of the article imagable upon exposure to intense radiation.

As a result, a wide variety of different articles can be rendered imagable. For example, articles which are made from natural or synthetic resins, such as molded or extruded articles, films, coating compositions, such as paints and inks, and potting compounds can be prepared in accordance with the present invention. In addition, glass or ceramic articles or coatings can be rendered imagable.

In accordance with the process of the present invention, an image can be produced on a substrate by providing the substrate with a surface made of the composition of the present invention. Since the image is to be formed in the surface of the substrate, only the surface need be made of the present composition, although the entire substrate could be made of the composition.

The surface of the substrate to be imaged is then subjected to a source of intense radiant energy. Suitable sources of intense radiation include lasers, gas discharge lamps, such as xenon flash lamps, and the like. A pulsed TEA CO_2 laser with a wavelength of 10.6 microns, an inherent raw beam energy of 0.7 joule/cm.^{2}, and a pulse duration of 100 nanoseconds, operated at 28-32 KV and optically focused at a reduction of between 2.0:1 and 2.5:1, has been found to be particularly suitable. The surface of the substrate should be exposed to a source of radiation having a sufficient energy density for a period of time sufficient to produce an image in the areas exposed to the intense radiation. An energy density of from about 0.7 to about 6.0 joules/cm.^{2} has been found to be suitable.

The substrate typically is exposed to the source of radiation in the pattern of the image to be produced in the surface. Only those areas of the substrate on which an image is desired are subjected to the radiation. This imagewise exposure can be achieved, for example, using a mask, stencil, or other similar means for producing a pattern.

Upon exposure of the substrate to the imagewise pattern of intense radiation, the surface of the substrate changes color in the areas exposed to produce the desired image. If the binder material for the clay and barium sulfate is substantially transparent and colorless, then the image produced will appear white by contrast. If, however, the binder is made of a material that changes color or contains a dye or pigment which wholly or partially masks the image, then the image will appear as white or as a lighter shade of the color of the binder in contrast to a dark background, due to the underlying white image. For example, if the clay and barium sulfate were in an acrylic binder material, a clear colorless coating would be produced. If this material were coated onto a black article and then the coating is exposed to intense radiation, a white image would be produced against a black background. If, instead, a phenolic binder material were employed, a clear colorless coating would be obtained that would become yellow upon exposure to the radiation because the phenolic material exposed would change color from clear to yellow, thereby rendering the otherwise white image yellow in color. The phenolic coating that was not exposed to the radiation would remain clear so that the image would appear yellow against the black background.

If the contrast of the image produced is less than that desired, it can be improved by adjusting the amount of the clay and barium sulfate in the binder, the energy density of the source of intense radiation, the duration of the exposure to the radiation, and the color of the binder material or of the background against which the image is produced.

A more complete appreciation of the present invention will be realized by reference to the following specific examples which relate to specific imagable compositions and to methods for preparing such compositions. Unless otherwise indicated, all references to percent or to parts of ingredients are to percent by weight and parts by weight of those ingredients. The following examples are not intended to limit the invention disclosed herein except to the extent that limitations are specifically stated or to the extent that limitations appear in the appended claims. It will be apparent to those skilled in the art that modifications or substitutions can be made to the present invention, such as those suggested in the foregoing detailed description without departing from the spirit and scope of the invention.

EXAMPLE 1

An epoxy resin premix was prepared by mixing about 45.5 parts of an epoxy solution containing about 54.2 percent of a bisphenol A glycidyl ether epoxy resin and about 45.8 percent of tributyl phosphate, about 43.1 parts of a solution containing about 60 percent of a cross-linking resin for the epoxy and about 40 percent of tributyl phosphate, about 6 parts of a solution containing about 80 percent of a heat activated curing agent for the epoxy and about 20 percent of tributyl phosphate, about 3.2 parts of a thixotropic bodying agent, about 1.4 parts of an adhesion promoter, and about 0.7 parts of a fungicide using a high speed disk disperser set at a disk tip speed of 600 ft/min.

A black, heat curable coating composition was then prepared by mixing 50 grams of the above premix with 75 grams of barium sulfate, 30 grams of titanium dioxide, and 15 grams of graphite.

The mixture was then transferred to a three-roll mill for processing twice through the mill.

A portion of the coating composition was then coated over the surface of the potting compound of an electronic component at a wet thickness of 0.75 to 1.0 mil using a Markem Model 20A body coating apparatus. The coated electronic component was then heated to cure the coating. The cured coating comprised about 49.9 percent of barium sulfate, about 19.9 percent of titanium dioxide, about 10 percent of graphite and about 20.2 percent of epoxy binder.

The coated electronic component was then exposed to a pulsed TEA CO_2 laser for the duration of one laser pulse. The laser was operated at 30 KV with a 2:1 beam reduction and produced an energy density of 2.5 joules/cm.^{2}. The duration of the laser pulse was 100 nanoseconds. A metal imaging stencil was placed in the path of the laser beam. A white image was produced in the black coating which corresponded to the pattern in the stencil.

EXAMPLE 2

A black, heat curable coating composition was prepared by mixing 30 grams of the epoxy resin premix prepared in Example 1 above with 5 grams of a mineral black which contained a small amount of a carbon black mordanted onto clay following the procedure of Example 1.

The composition was then coated onto The potting compound for an electronic component and cured. The cured coating comprised about 21.5 percent of the mineral black and about 78.5 percent of the epoxy resin binder.

The coated electronic component was then exposed to an imagewise pattern of laser radiation. A white image was produced in the black coating in the areas exposed to the laser radiation.

EXAMPLE 3

Following the procedure of Example 1 above, a black coating composition was prepared by mixing 30 grams of the epoxy resin premix of Example 1 with 2 grams of mineral black and 10 grams of barium sulfate.

The composition was then coated onto an electronic component potting compound and cured. The cured coating comprised about 6.6 percent of the mineral black, about 33.1 percent of the barium sulfate and about 60.3 percent of the epoxy resin binder.

The coated potting compound was then exposed to an imagewise pattern of laser radiation. A white image was produced in the very transparent black coating in the areas exposed to the laser radiation.

EXAMPLE 4

Following the procedure of Example 1 above, a black coating composition was prepared by mixing 30 grams of the epoxy resin premix of Example 1 with 5 grams of mineral black and 10 grams of barium sulfate.

The composition was then coated onto an electronic component potting compound and cured. The cured coating comprised about 15.1 percent of mineral black, about 30.1 percent of barium sulfate and about 54.8 percent of the epoxy resin binder.

The coated potting compound was then exposed to an imagewise pattern of laser radiation. A fair to good white image was produced in the coating in the areas exposed to the laser radiation.

EXAMPLE 5

Following the procedure of Example 1 above, a black coating composition was prepared by mixing 30 grams of the epoxy resin premix of Example 1 with 7 grams of mineral black and 20 grams of barium sulfate.

The composition was then coated onto an electronic component potting compound and cured. The cured coating comprised about 15.5 percent of mineral black, about 44.2 percent of barium sulfate and about 40.3 percent of the epoxy resin binder.

A fair white image was produced in the coating in the areas exposed to an imagewise pattern of laser radiation.

EXAMPLE 6

Following the procedure of Example 1 above, a black coating composition was prepared by mixing 57 grams of the coating composition prepared in Example 5 with 20 grams of a urea-formaldehyde resin.

The composition was then coated onto an electronic component potting compound and cured. The cured coating comprised about 10.7 percent of mineral black, about 30.7 percent of barium sulfate, and about 58.6 percent of epoxy and urea-formaldehyde resin binder.

The coated potting compound was then exposed to an imagewise pattern of laser radiation. A very good white image was produced in the coating in the areas exposed to the laser radiation.

EXAMPLE 7

Following the procedure of Example 1 above, a black coating composition was prepared by mixing 30 grams of the epoxy resin premix of Example 1 with 30 grams of a urea-formaldehyde resin, 7 grams of a mineral black and 40 grams of barium sulfate.

The composition was then coated onto an electronic component potting compound and cured. The cured coating comprised about 7.4 percent of mineral black, about 42.0 percent of barium sulfate and about 50.6 percent of epoxy and urea-formaldehyde resin binder.

An excellent white image was produced in the coating in the areas exposed to an imagewise pattern of laser radiation.

EXAMPLE 8

Following the procedure of Example 1 above, a black coating composition was prepared by mixing 30 grams of the epoxy resin premix of Example 1 with 30 grams of a urea-formaldehyde resin, 30 grams of a mineral black and 30 grams of barium sulfate.

The composition was coated onto an electronic component potting compound and then cured. The cured coating comprised about 27.7 percent of the mineral black, about 27.7 percent of the barium sulfate and about 44.6 percent of the epoxy and urea-formaldehyde resin binder.

An image was not produced upon exposure of the coating to laser radiation. The composition contained too much black pigment that masked the image.

EXAMPLE 9

Following the procedure of Example 1 above, a black coating composition was prepared by mixing 30 grams of the epoxy resin premix of Example 1 with 3 grams of a mineral black, 3 grams of a mineral violet pigment and 30 grams of barium sulfate.

The composition was then coated onto an electronic component potting compound and cured. The cured coating comprised about 5.5 percent of the mineral black, about 55.3 percent of the barium sulfate, about 5.5 percent of the violet pigment, and about 33.6 percent of the epoxy resin binder.

The coated potting compound was then exposed to an imagewise pattern of laser radiation. A white image having excellent color and contrast was produced in the coating in the areas exposed to the laser radiation.

EXAMPLE 10

Following the procedure of Example 1 above, a coating composition was prepared by mixing 10 grams of the coating composition prepared in Example 9 above with 5 grams of a urea-formaldehyde resin.

The composition was coated onto an electronic component potting compound and cured. The cured composition comprised about 3.7 percent of the mineral black, about 36.9 percent of the barium sulfate, about 3.7 percent of the violet pigment, and about 55.7 percent of the epoxy and urea-formaldehyde resin binder.

The coated potting compound was then exposed to an imagewise pattern of laser radiation. An excellent white image was produced in a very transparent black coating in the areas exposed to the laser radiation.

EXAMPLE 11

Following the procedure of Example 1 above, a black coating composition was prepared by mixing 40 grams of the coating composition prepared in Example 9 above with 40 grams of a urea-formaldehyde resin and 20 grams of a water-washed kaolin clay (ASP 170, Engelhard Minerals & Chemicals).

The composition was coated onto an electronic component potting compound and then cured by heating for 2 hours at 150°C. The cured coating comprised about 1.9 percent of the mineral black, about 21.5 percent of the clay, about 19.6 percent of the barium sulfate, about 1.9 percent of the violet pigment, and about 55 percent of the epoxy and urea-formaldehyde resin binder.

A white image having excellent contrast was produced in the very transparent black coating in the areas exposed to an imagewise pattern of laser radiation.

EXAMPLE 12

Following the procedure of Example 1 above, a clear coating composition was prepared by mixing 20 grams of the epoxy resin premix prepared in Example 1 with 40 grams of a urea-formaldehyde resin, 20 grams of a water-washed kaolin clay (ASP 170), and 20 grams of barium sulfate.

The composition was coated onto an electronic component potting compound and then cured. The cured coating comprised about 21.7 percent of the clay, about 21.7 percent of barium sulfate, and about 56.5 percent of the epoxy and urea-formaldehyde resin binder.

The coated potting compound was then exposed to an imagewise pattern of laser radiation. A white image having excellent contrast was produced in the transparent coating in the areas exposed to the laser radiation.

EXAMPLE 13

A heat curable coating composition was prepared by mixing 40 grams of a water-washed kaolin clay (ASP 170) and 40 grams of a urea-formaldehyde resin following the procedure of Example 1 above.

The mixture was coated onto an electronic component potting compound and heat cured. The coating became white upon curing. The cured coating comprised 50 percent clay and 50 percent urea-formaldehyde resin binder. It is believed that the index of refraction of the binder became less than that of the clay upon curing of the coating.

EXAMPLE 14

Following the procedure of Example 1 above, a heat curable coating composition was prepared by mixing 20 grams of the epoxy resin premix prepared in Example 1 with 40 grams of a urea-formaldehyde resin and 80 grams of a water-washed kaolin clay (ASP 170).

The composition was coated onto an electronic component potting compound and heat cured. The coating became white upon curing like the coating of Example 13 above. The cured coating comprised about 60.5 percent of the clay and about 39.5 percent of the epoxy and urea-formaldehyde resin binder. It is believed that the index of refraction of this binder likewise became less than that of the clay upon curing of the coating.

EXAMPLES 15-16

Two heat curable coating compositions were prepared by mixing 40 grams of the epoxy resin premix prepared in Example 1 with each of 20 grams and 30 grams of a water-washed kaolin clay (ASP 170), respectively, following the procedure of Example 1 above.

Each composition was then coated onto an electronic component potting compound and cured. Both cured coatings were essentially transparent. The first cured coating comprised about 45.2 percent of the clay and about 54.8 percent of the epoxy resin binder. The second cured coating comprised about 55.3 percent of the clay and about 44.7 percent of the epoxy resin binder.

The coated potting compounds were then exposed to an imagewise pattern of laser radiation. A very good white image was produced in the first coating and a good white image was produced in the second coating that was not as bright white as the image produced in Example 12 above.

EXAMPLES 17-19

Following the procedure of Example 1 above, three heat curable coating compositions were prepared by mixing 20 grams of a water-washed kaolin clay (ASP 170) and 20 grams of barium sulfate with each of 40 grams, 50 grams and 60 grams, respectively, of the epoxy resin premix prepared in Example 1 above.

Each composition was then coated onto an electronic component potting compound and cured. All of the cured coatings were essentially transparent. The first cured coating comprised about 31.1 percent of the clay, about 31.1 percent of the barium sulfate, and about 37.8 percent of the epoxy resin binder. The second cured coating comprised about 28.4 percent of the clay, about 28.4 percent of the barium sulfate, and about 43.2 percent of the epoxy resin binder. The third cured coating comprised about 26.2 percent of the clay, about 26.2 percent of barium sulfate, and about 47.6 percent of the epoxy resin binder.

The three coated potting compounds were each exposed to an imagewise pattern of laser radiation. The white image produced in the first coating was excellent. The coating was very flat and not glossy. An excellent white image was produced in the second coating. An excellent white image was also produced in the third coating, although it was not quite as good as the image produced in Example 12 above.

EXAMPLE 20

Following the procedure of Example 1 above, a heat curable coating composition was prepared by mixing 50 grams of the epoxy resin premix prepared in Example 1 with 40 grams of a water-washed kaolin clay (ASP 170).

The composition was then coated onto an electronic component potting compound and cured. The cured coating was essentially transparent and comprised about 56.9 percent of the clay and about 43.1 percent of the epoxy resin binder.

The coated potting compound was then exposed to an imagewise pattern of laser radiation. A good white image was produced in the coating, although it was not clear and bright.

EXAMPLE 21

Following the procedure of Example 1 above, a heat curable coating composition was prepared by mixing 50 grams of the epoxy resin premix prepared in Example 1 with 40 grams of barium sulfate.

The composition was coated onto an electronic component potting compound and then cured. The cured coating was essentially transparent and comprised about 56.9 percent of barium sulfate and about 43.1 percent of the epoxy resin binder.

A good bright white image was produced in the coating upon exposure to an imagewise pattern of laser radiation. A higher energy density than that of Example 20 above was required to produce the good image when the barium sulfate was substituted for the clay.

EXAMPLE 22

Following the procedure of Example 1 above, a heat curable coating composition was prepared by mixing 50 grams of the epoxy resin premix of Example 1 with 50 grams of a water-washed kaolin clay (ASP 170).

The mixture was coated onto an electronic component potting compound and then heat cured. The cured coating was essentially transparent and comprised about 62.2 percent of the clay and about 37.8 percent of the epoxy resin binder.

The coated potting compound was then exposed to an imagewise pattern of laser radiation which produced very good white prints in the areas of the coating exposed to the radiation.

EXAMPLE 23

A U.V. curable acrylated epoxy resin premix was prepared by mixing 18 parts of a mixture containing about 51.5 percent by weight of an acrylic U.V. curable resin, about 44.4 percent by weight of an acrylated epoxy resin, about 2.3 percent by weight of a plasticizer and about 1.7 percent by weight of an adhesion promoter with 1.5 parts of a U.V. photoinitiator.

A U.V. curable coating composition was then prepared by mixing 50 grams of the above premix with 20 grams of a water-washed kaolin clay (ASP 170) and 20 grams of barium sulfate.

The composition was then coated onto the surface of an electronic component potting compound to a wet thickness of 0.75 to 1.0 mil using a Markem Model 20A body coating apparatus. The coated electronic component was then conveyed under a 200 Watt/in ultraviolet lamp fixed at a distance of 2 inches above the component for a distance of 7.5 inches and a cure rate of 40 ft/min. The cured composition was essentially transparent and comprised about 22.2 percent of the clay, about 22.2 percent of barium sulfate, and about 55.6 percent of the acrylated epoxy resin binder.

The coated potting compound was then exposed to an imagewise pattern of laser radiation. The beam of a pulsed TEA CO_2 laser at 30 KV having a 2.5:1 reduction and an energy density of 2.5 joules/cm.^{2} was attenuated by a metal imaging stencil. A fair white image was produced in the coating.

EXAMPLE 24

Following the procedure of Example 1 above, a heat curable coating composition was prepared by mixing 50 grams of the epoxy resin premix of Example 1 with 10 grams of a urea-formaldehyde resin, 25 grams of a water-washed kaolin clay (ASP 170) and 25 grams of barium sulfate.

The composition was coated onto a potting compound and then heat cured. The cured coating was essentially transparent and comprised about 27.7 percent of the clay, about 27.7 percent of barium sulfate, and about 44.6 percent of the epoxy and urea-formaldehyde resin binder.

The coated potting compound was then exposed to an imagewise pattern of laser radiation. A white image was produced in the areas exposed to the radiation that was poorer than the image produced in Example 17 above.

EXAMPLE 25

Following the procedure of Example 23 above, a U.V. curable coating composition was prepared by mixing 50 grams of the acrylated epoxy resin premix of Example 23 with 15 grams of a water-washed kaolin clay (ASP 170) and 15 grams of barium sulfate.

The composition was then coated onto an electronic component potting compound and cured by exposure to U.V. radiation. The cured coating was essentially clear and comprised about 18.75 percent of the clay, about 18.75 percent of barium sulfate, and about 62.5 percent of the acrylated epoxy resin binder.

The coated potting compound was then exposed to an imagewise pattern of laser radiation. A white image was produced in the coating that did not exhibit good contrast.

EXAMPLES 26-27

Following the procedure of Example 23 above, a U.V. curable premix was prepared by mixing 37.1 percent of a novolac epichlorohydrin phenol formaldehyde epoxy resin, 37.1 percent of a cycloaliphatic epoxy resin, 24.3 percent of a U.V. epoxy curative, and 1.4 percent of an adhesion promoter.

Two U.V. curable coating compositions were then prepared by mixing 50 grams of the above premix, 40 grams of barium sulfate, 1 gram of a U.V. fluorescing whitener and 2 grams of a wax with each of 5 grams and 15 grams of a water-washed kaolin clay (ASP 170), respectively.

Each of the two compositions was then coated onto an electronic component potting compound and cured by exposure to U.V. radiation. Both cure coatings were essentially transparent.

The first cured coating comprised about 5.1 percent of the clay, about 40.8 percent of barium sulfate, about 1.0 percent of the U.V. fluorescing whitener, about 2.1 percent of the wax, and about 51.0 percent of the epoxy resin binder. The second coating comprised about 13.9 percent of the clay, about 37.0 percent of barium sulfate, about 0.9 percent of the fluorescing whitener, about 1.9 percent of the wax, and about 46.3 percent of the epoxy resin binder.

Both coated potting compounds were then exposed to an imagewise pattern of laser radiation. White images were produced in both coatings.

EXAMPLES 28-30

Following the procedure of Example 23 above, three U.V. curable coating compositions were prepared by mixing 50 grams of the epoxy resin premix of Example 26, 60 grams of barium sulfate, 2 grams of a fluorescing whitener and 2 grams of a wax with 15 grams of each of three different water-washed kaolin clays (ASP 170, 602, 072, Engelhard Minerals & Chemicals).

Each of the three compositions was coated onto an electronic component potting compound and then cured by exposure to U.V. radiation. All of the cured coatings were essentially transparent and comprised about 11.6 percent of the clay, about 46.5 percent of barium sulfate, about 1.6 percent of the fluorescing whitener, about 1.6 percent of the wax, and about 38.7 percent of the epoxy resin binder.

The coated potting compounds were then exposed to an imagewise pattern of laser radiation. Excellent white images were produced in all three coatings.

EXAMPLE 31

Following the procedure of Example 23 above, a U.V. curable coating composition was prepared by mixing 50 grams of the epoxy resin premix of Example 26 with 160 grams of barium sulfate. The ingredients were stirred together and passed through a three-roll mill once.

The composition was then coated onto an electronic component potting compound and cured by exposing the coating to a 1500 Watt ultraviolet lamp at 200 Watts/in at a rate of 50 ft/min. The cured coating was essentially transparent and comprised about 76.2 percent of barium sulfate and about 23.8 percent of the epoxy resin binder.

The coated potting compound was then exposed to an imagewise pattern of laser radiation using a pulsed TEA CO_2 laser at 31 KV, a reduction of 2:1 and an energy density of 2.5 joules/cm.^{2}. A grayish metallic white image was produced that was not as bright as the images produced in compositions containing both clay and barium sulfate.

EXAMPLE 32

A potting compound suitable for encapsulating electronic components was prepared by mixing 25 grams of a bisphenol A glycidyl ether epoxy resin with 7.5 grams of a water-washed kaolin clay (ASP 170) and 30 grams of barium sulfate. The compound was molded and then cured. The compound comprised about 12 percent of the clay, about 48 percent barium sulfate, and about 40 percent of epoxy resin.

The potting compound was then exposed to an imagewise pattern of laser radiation using a pulsed TEA CO_2 laser at 31 KV, a reduction of 2:1, and an energy density of 2.5 joules/cm.^{2}. A good clear white image was produced in the surface of the potting compound. Higher concentrations of the clay and barium sulfate would improve the uniformity of the image.

EXAMPLE 33

A potting compound suitable for encapsulating electronic components was prepared by mixing 0.5 grams of a violet pigment with 62.5 grams of the potting compound prepared in Example 32 above. The compound was molded and then cured. The compound was violet in color and comprised about 11.9 percent of the clay, about 47.6 percent of the barium sulfate, about 0.8 percent of the violet pigment, and about 39.7 percent of the epoxy resin binder.

The potting compound was then exposed to an imagewise pattern of laser radiation. A white image was produced in the violet compound. Contrast of the image could be improved by the addition of more clay and barium sulfate to the compound.

EXAMPLE 34

Following the procedure of Example 1 above, a heat curable coating composition was prepared by mixing 50 grams of the epoxy resin premix of Example 1 with 15 grams of a water-washed kaolin clay (ASP 170), 60 grams of barium sulfate, 2 grams of a fluorescing whitener, and 2 grams of a polyethylene wax.

The composition was then coated onto an electronic component potting compound and cured by exposure to I.R. radiation. The cured coating was essentially transparent and comprised about 13.7 percent of the clay, about 54.9 percent of barium sulfate, about 1.8 percent of fluorescing whitener, about 1.8 percent of the wax, and about 27.8 percent of the epoxy resin binder.

The coated potting compound was then exposed to an imagewise pattern of laser radiation. A clear white image was produced in the coating.

EXAMPLE 35

Following the procedure of Example 1 above, a heat curable coating composition was prepared by mixing 50 grams of a phenolic resin premix comprising 49.7 percent of a reactive phenolic resin 49.7 percent tributyl phosphate, and 0.6 percent of a fungicide with 25 grams of a water-washed kaolin clay (ASP 170), 60 grams of barium sulfate, 2 grams of a fluorescing whitener, and 2 grams of a polyethylene wax.

The composition was coated onto an electronic component potting compound and heat cured. The cured coating was essentially transparent and comprised about 14.4 percent of the clay, about 57.6 percent of barium sulfate, about 1.9 percent of fluorescing whitener, about 1.9 percent of the wax and about 24.2 percent of phenolic resin binder.

The coated potting compound was then exposed to an imagewise pattern of laser radiation. A sharp yellow image was produced in the areas of the coating exposed to the radiation. The phenolic resin binder changed color to yellow upon exposure to the radiation, so that the white image produced in the coating appeared yellow through the yellow binder.

EXAMPLE 36

A varnish premix was prepared by mixing 16 parts by volume of a varnish solution comprising 86.8 percent of a phenol modified tung oil, 12.4 percent of carbitol acetate and 0.8 percent of an anti-skinning agent, 0.25 part of cobalt and manganese driers and 0.5 part of a fungicide.

Following the procedure of Example 1 above, an air cured coating composition was prepared by mixing 50 grams of the above premix with 15 grams of a water-washed kaolin clay (ASP 170), 60 grams of barium sulfate, 2 grams of fluorescing whitener and 2 grams of a polyethylene wax.

The composition was then coated onto an electronic component potting compound and dried. The coating was essentially transparent and comprised about 12.4 percent of the clay, about 49.4 percent of barium sulfate, about 1.6 percent of fluorescing whitener, about 1.6 percent of the wax, and about 34.9 percent of varnish binder.

The coated potting compound was then exposed to an imagewise pattern of laser radiation. A light white image was produced in the coating in the areas exposed. The energy density of the laser could have been increased to improve the contrast of the image.

EXAMPLE 37

Following the procedure of Example 1 above, a coating composition was prepared by mixing 50 grams of a 20% solution of nitrocellulose with 15 grams of a water-washed kaolin clay (ASP 170), 60 grams of barium sulfate, 2 grams of fluorescing whitener and 2 grams of a polyethylene wax.

The composition was then coated onto an electronic component potting compound and dried. The dried coating was milky white and comprised about 16.8 percent of the clay, about 67.4 percent of barium sulfate, about 2.3 percent of fluorescing whitener, about 2.3 percent of the wax, and about 11.2 percent of nitrocellulose binder.

The coated potting compound was then exposed to an imagewise pattern of laser radiation. The coating was burned off in the areas exposed to the radiation. The coating was not transparent because the concentration of the clay and barium sulfate was so high.

EXAMPLE 38

A ceramic coating composition was prepared by mixing 12 grams of a drying oil modified alkyd resin, 2 grams of a water-washed kaolin clay (ASP 170), 6 grams of barium sulfate, 10 grams of glass frit (Mason flux #10) and 4 grams of lithium fluoride using the procedure of Example 1.

The composition was then coated onto a sheet of glass and heated to 1200°F for 3 minutes. The resin was completely burned off during heating of the coating. The coating produced was transparent and comprised about 9.1 percent of the clay, about 27.3 percent of barium sulfate, about 45.4 percent of glass and about 18.2 percent of lithium fluoride.

The ceramic coating was then exposed to an imagewise pattern of laser radiation using a pulsed TEA CO_2 laser at 31 KV, a 2:1 reduction, and an energy density of 2.5 joules/cm.^{2}. A white image of low contrast was produced in the ceramic coating.

EXAMPLE 39

Following the procedure of Example 26 above, 25 grams of a calcined kaolin clay (Satintone No. 5, Engelhard Minerals & Chemicals) was mixed with 50 grams of the epoxy resin premix prepared in Example 26 using three passes through a three-roll mill. The viscosity at 80°F was 300,000 cps.

The composition was coated by hand onto a stick of molded potting compound used for encapsulating electronic components. The coating was cured by exposure to U.V. radiation. The cured coating was essentially transparent and comprised about 33.3 percent of the calcined clay and about 66.7 percent of the epoxy resin binder.

The coated potting compound was then exposed to an imagewise pattern of laser radiation using a pulsed TEA CO_2 laser at 30 KV, a 2:1 reduction, and an energy density of 2.6 joules/cm.^{2}. A white image was produced in the coating in the areas exposed to the radiation.

EXAMPLE 40

A coating composition was prepared following the procedure of Example 39 above with the exception that the calcined kaolin clay was replaced with an equal amount of a water-washed kaolin clay (ASP 170). The viscosity of the mixture at 83°F was 66,000 cps.

The composition was coated onto an electronic component potting compound and cured. The cured coating was essentially transparent and comprised about 33.3 percent of the water-washed clay and about 66.7 percent of the epoxy resin binder.

The coated potting compound was then exposed to an imagewise pattern of laser radiation. A bright white image was produced in the areas exposed to the radiation.

WHAT IS CLAIMED IS:

1. A radiation imagable composition in which an image can be produced upon exposure to intense radiation, said composition comprising

(a) at least one component selected from the group consisting of clay and barium sulfate, and

(b) a binder material which will not be destroyed during exposure of the composition to intense radiation and will not mask the image produced upon exposure to intense radiation.

2. The composition of claim 1 wherein the binder material comprises a natural or synthetic resin material.

3. The composition of claim 1 wherein the binder material comprises a glass, ceramic or vitreous material.

4. The composition of claim 1 wherein the binder material has an index of refraction greater than the index of refraction of the clay or of the barium sulfate.

5. The composition of claim 4 wherein the composition is essentially transparent or translucent when dried or cured.

6. The composition of claim 1, 4 or 5 wherein the image produced is white in color.

7. The composition of claim 2 wherein the binder material comprises an epoxy resin.

8. The composition of claim 2 wherein the binder material comprises an acrylic resin.

9. The composition of claim 2 wherein the binder material comprises a urea-formaldehyde resin.

10. The composition of claim 2 wherein the binder material comprises a phenolic resin.

11. The composition of claim 10 wherein the image produced is yellow in color.

12. The composition of claim 1 which comprises up to about 65 percent by weight of clay.

13. The composition of claim 12 which comprises from about 15 to about 35 percent by weight of clay.

14. The composition of claim 1 which comprises up to about 80 percent by weight of barium sulfate.

15. The composition of claim 14 which comprises from about 25 to about 50 percent by weight of barium sulfate.

16. The composition of claim 1 or 4 which comprises from about 3 to about 35 percent by weight of clay and from about 15 to about 60 percent by weight of barium sulfate.

17. A coating composition comprising a radiation imagable composition according to any of claims 1-16.

18. A molding compound comprising a radiation imagable composition according to any of claims 1-16.

19. A potting compound for encapsulating an electronic component comprising a radiation imagable composition according to any of claims 1-16.

20. An electronic component encapsulated in a potting compound, said potting compound comprising a radiation imagable composition according to any of claims 1-3, 7 and 12-16.

21. An electronic component encapsulated in a potting compound, said potting compound being coated with a radiation imagable composition according to any of claims 1-16.

22. A process for producing an image on a substrate comprising

(a) providing a substrate made of a radiation imagable composition in which an image can be produced upon exposure to intense radiation, said composition comprising

(1) at least one component selected from the group consisting of clay and barium sulfate, and

(2) a binder material which will not be destroyed during exposure of the composition to intense radiation and will not mask the image produced upon exposure to intense radiation, and

(b) exposing the surface of said substrate to a source of high intensity radiation having a sufficient energy density and for a period of time sufficient to produce an image in the areas exposed to intense radiation.

23. A process for producing an image on a substrate comprising

(a) providing a substrate,

(b) coating said substrate with a radiation imagable composition in which an image can be produced upon exposure to intense radiation, said composition comprising

(1) at least one component selected from the group consisting of clay and barium sulfate, and

(2) a binder material which will not be destroyed during exposure of the composition to intense radiation and will not mask the image produced upon exposure to intense radiation, and

(c) exposing the surface of said coating to a source of high intensity radiation having a sufficient energy density for a period of time sufficient to produce an image in the areas exposed to the radiation.

24. A process for rendering a substrate imagable upon exposure to intense radiation which comprises making said substrate from a composition comprising

(a) at least one component selected from the group consisting of clay and barium sulfate, and

(b) a binder material which will not be destroyed during exposure to intense radiation and will not mask the image produced upon exposure to intense radiation.

25. A process for rendering a substrate imagable upon exposure to intense radiation which comprises coating said substrate with a composition comprising

(a) at least one component selected from the group consisting of clay and barium sulfate, and

(b) a binder material which will not be destroyed during exposure to intense radiation and will not mask the image produced upon exposure to intense radiation.

26. The process of claim 22 or 23 wherein the source of radiation is a laser.

27. The process of claim 26 wherein said laser employs carbon dioxide gas as the active laser medium.

28. The process of claim 22 or 23 wherein the source of radiation is a gas discharge lamp.

29. The process of claim 28 wherein the gas discharge lamp is a xenon flash lamp.

30. The process of claim 22 or 23 wherein the source of radiation has an energy density of about 0.7 to about 6.0 joules/cm.^{2}.

31. The process of claim 22, 23, 24 or 25 wherein the binder material comprises a natural or synthetic resin material.

32. The process of claim 22, 23, 24 or 25 wherein the binder material comprises a glass, ceramic or vitreous material.

33. The process of claim 22, 23, 24 or 25 wherein the binder material has an index of refraction greater than the index of refraction of the clay or of the barium sulfate.

34. The process of claim 33 wherein the radiation imagable composition is essentially transparent or translucent when dried or cured.

35. The process of claim 22, 23, 24, 25 or 33 wherein the image produced is white in color.

36. The process of claim 31 wherein the binder material comprises an epoxy resin.

37. The process of claim 31 wherein the binder material comprises an acrylic resin.

38. The process of claim 31 wherein the binder material comprises a urea-formaldehyde resin.

39. The process of claim 31 wherein the binder material comprises a phenolic resin.

40. The process of claim 39 wherein the image produced is yellow in color.

41. The process of claim 22, 23, 24 or 25 wherein the radiation imagable composition comprises up to about 65 percent by weight of clay.

42. The process of claim 41 wherein the radiation imagable composition comprises from about 15 to about 35 percent by weight of clay.

43. The process of claim 22, 23, 24 or 25 wherein the radiation imagable composition comprises up to about 80 percent by weight of barium sulfate.

44. The process of claim 43 wherein the radiation imagable composition comprises from about 25 to about 50 percent by weight of barium sulfate.

45. The process of claim 22, 23, 24 or 25 wherein the radiation imagable composition comprises from about 3 to about 35 percent by weight of clay and from about 15 to about 60 percent by weight of barium sulfate.