Dec. 25, 1945. S. ISENBERG 2,391,705

PRINTING METHOD AND PRODUCT

Filed Aug. 10, 1942

Fig. 1.

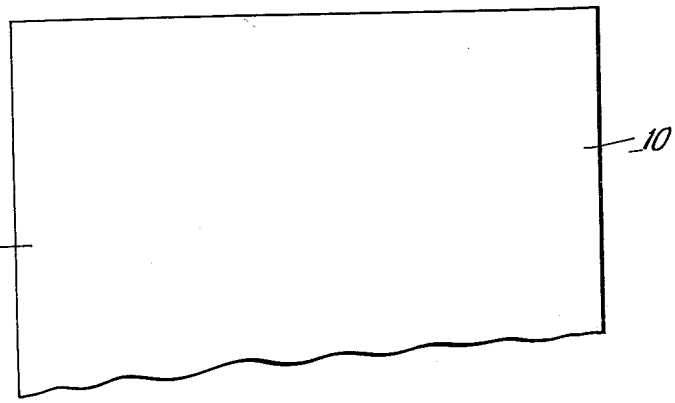


Fig. 2.

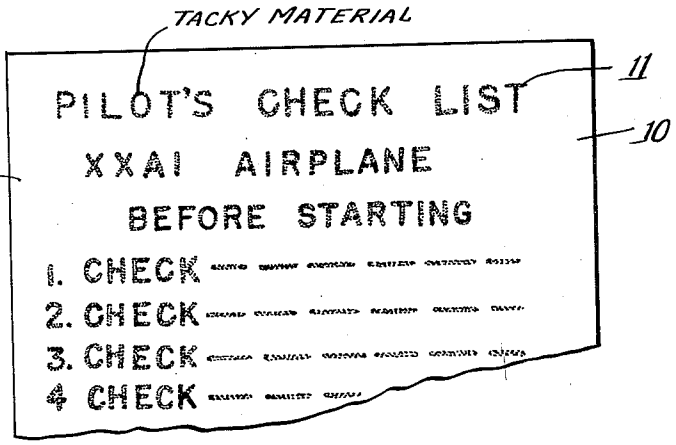
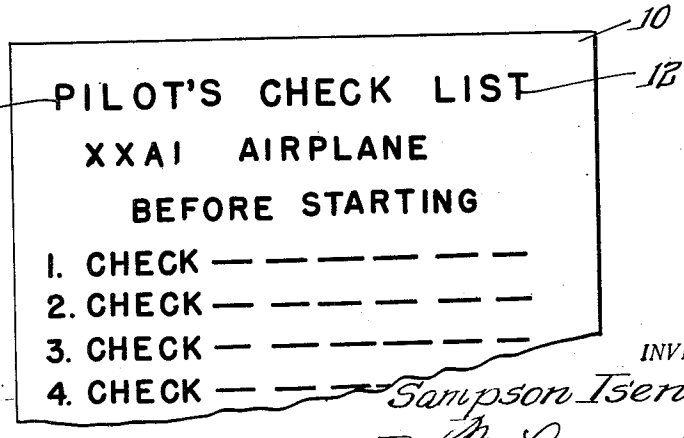


Fig. 3.



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Patented Dec. 25, 1945 2,391,705

UNITED STATES PATENT OFFICE

2,391,705

PRINTING METHOD AND PRODUCT

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Application August 10, 1942, Serial No. 454,291

12 Claims. (Cl. 40—134)

My invention relates to the application of luminescent materials to paper surfaces and the like. It relates more in particular to a method of applying characters to a surface, the characters being visible in both daylight and ultraviolet light, by a process involving printing. The invention is also concerned with a new article of manufacture produced as a result of the method, this new article comprising, for example, a dial, map, table top, book, direction card, marker or the like, adapted to be seen in either daylight or under ultra violet light.

One embodiment of the invention is disclosed in the accompanying drawing wherein

Fig. 1 is a part of a sheet of paper on which are to be applied characters comprising luminescent material;

Fig. 2 shows the same sheet on which the essential printing has been made; and

Fig. 3 shows the completed article after it has been dusted with the specially prepared luminescent pigment.

At times it is desirable to produce, in an accurate but inexpensive manner, an article containing applied characters which are visible both in ultra violet light and in daylight. The present armed conflict has increased the demand for such articles very greatly. Heretofore no fully satisfactory method has been available for producing such articles inexpensively and acceptable so far as their ultra violet response is concerned. Attempts have been made to introduce luminescent pigments into printing inks and run the inks on ordinary presses to produce a printed copy. So far as I know, a satisfactory product has not been produced by this means.

In order to produce a suitable desired product, I conceived that good results could be obtained if the luminescent material were applied to a printed surface by a dusting procedure. I further found that I could readily obtain a more highly luminescent character by means of the dusting method; but problems occurred, principally in the ability to obtain a sharp line between the edge of the printed character and the unprinted surface and in the fact that the powdered luminescent material would tend to adhere to the entire surface of the paper or other material on which the printed characters were applied. This problem of adherence I found particularly troublesome due to the fact that the paper selected preferably was one which produced as little glare of reflected light as possible. A very dull black surface was found preferable so far as light reflection was concerned and the tendency of the powdered luminescent material to adhere to this type of surface is particularly marked.

I overcame the problems identified primarily by utilizing in a particular way, with the luminescent material, a chemical compound in the form of a partial ester of a polyhydric alcohol as hereinafter more particularly described, the result being that adherence to a previously applied tacky surface was promoted and adherence to the paper surface was substantially entirely eliminated. The utilization of the partial ester, in a manner to be described, also has the property of limiting the effect of weathering, particularly the marked tendency of a combination of light and moisture to destroy the efficacy of certain types of compounds having luminescent properties.

In carrying out my invention, I first treat the paper surface by means of a printing operation to apply a base coat on which the luminescent material is dusted. With certain types of paper a layer of clear printing varnish is first applied under the base coat. In any event, the base coat is applied in such a way that clear sharp outlines of the printed characters are obtained. The base coat, the nature of which will be referred to later, comprises a tacky sizing material to which a powdered luminescent material will readily adhere. The term "tacky," of course, is used in a relative sense, it being merely necessary that the printed surface be sufficiently tacky or sticky at the time the luminescent material is dusted thereon so that there will be no question of adherence of sufficient particles of luminescent material to produce, in effect, a layer of luminescent material above the base coat. The base coat may be any suitable ink-like material containing, for example, a drying oil, a thinner, a so-called extender when desired, and a coloring pigment. The coloring pigment may be metallic to increase by reflection the amount of ultra violet light delivered to the luminescent material; or it may be an ordinary pigment having a relation to the daylight and ultra violet color of the luminescent material employed.

The luminescent material may be any usual type of luminescent material, but preferably one which also will serve as a pigment and promote visibility of the applied characters during daylight. While many of the silicates and the like may be used to good advantage, I have found that among the most suitable luminescent materials to employ for my purpose are the sulphides, such as zinc or cadmium sulphide, or preferably

a mixed zinc cadmium sulphide activated with copper or the like.

The luminescent material is preferably —200 mesh. The particle size, however, is not critical so long as it is sufficiently pulverulent to be handled substantially as a powder and to adhere properly to the printed surface. The luminescent material is produced in a usual manner and is prepared for application to the printed surface, in accordance with my invention, in a special manner. The object is to associate it intimately with a partial ester but not to deprive it of its powder-like character, so that notwithstanding the presence of the partial ester it will behave as a true powder. One method is to triturate the luminescent material with the partial ester with a pestle and mortar or other suitable device which will have the effect of both comminuting and mixing. A preferred method is to introduce the luminescent material into a ball mill with the partial ester and a relatively low boiling point liquid with which the partial ester is miscible or in which it is soluble. In general, methyl alcohol, naphtha, benzol and like organic solvents may be used. The proportion of partial ester may be as high as 10% or 15% based upon the weight of the luminescent pigment, while as low as 2% may be employed with marked advantage. I find that on the average about 7% or 8% of partial ester will produce good results.

As an illustration of one manner of carrying out my invention, I wish to refer to the production of a large pamphlet or book containing in the neighborhood of two hundred pages, adapted for use by the United States Army and containing a very large amount of technical information, tables, conversion formulae and the like connected with certain kinds of military operations. It was desired that this book have a high degree of legibility not only in normal daylight but under ultra violet light. A paper was selected having a very dull black surface. This dull black surface was produced in ways known in the paper industry which need not be described in detail here. It is sufficient to point out that the surface exhibited considerable porosity and was quite absorbent. The first operation was to set the type for the book, using ordinary letter press equipment, and to print the characters with a clear printing varnish of a type known in the printing trade. This has the effect of sealing the paper at the places where the printed characters are to be applied, and avoids imparting a gloss to the paper, as would occur if the paper were sized completely in a customary manner. As the pages were printed, the varnish was dried in such manner as to avoid the necessity of slip sheeting, although I have found that slip sheeting may be employed to prevent offset from one varnished sheet to the other. The sheets were then printed with a base coat and the luminescent material dusted onto the base coat while still tacky. The base coat was made in the way a good sizing ink is made. I employed as ingredients boiled linseed oil, high boiling point thinner, such as "arabitol" and a drier such as cobalt naphthenate or manganese naphthenate. Zinc stearate was employed as a so-called extender and zinc sulphide employed as a pigment. The materials are mixed together in a manner usual to the printing art to produce an ink which prints well, but which has a somewhat tacky surface to which powdered luminescent material will adhere. This base coat dries partly by evaporation and partly by oxidation. It is colored to correspond with the luminescent material which is to be applied thereto. The base coat is applied with the same printing equipment, including the same type forms, used for applying the printing varnish, and usual methods of registering with the previously printed varnish are employed. The printed sheets are dusted with a luminescent material comprising a mixed zinc-cadmium sulphide activated with copper previously prepared to have a coating of glycerol mono-ricinoleate by a ball milling operation. The glycerol mono-ricinoleate comprises 7% by weight of the luminescent powder, the luminescent powder being ground fine enough to pass a 200 mesh screen. The luminescent zinc cadmium sulphide per se is produced in a way known in the art.

The prepared luminescent powder may be dusted on in various ways. I have obtained very good results by laying the sheets to which the base coat has been applied out on a table, and while the printed impressions are still tacky, merely dusting the previously prepared luminescent powder over the surface, using a hand screen. A soft brush or cloth is then used to wipe off the excess powder and this wiping action has the effect of somewhat more firmly embedding the luminescent material into the surface of the base coat. Compressed air may be used to blow off the excess powder. There is little or no tendency for the powder to adhere to the uncoated portion of the paper, whereas it adheres very readily to the base coat, and a sharp margin is obtained between the characters and the unprinted portion of the sheet. The printed and dusted sheets may be entirely sprayed with a solution of a synthetic resin, if desired, to furnish an additional protection to the printed characters. In general, however, this is not necessary. The printed pages are bound in an ordinary way known in the printing arts. In general, it is preferred that only one side of the sheets be printed, but if the practice of my invention is followed, there is no reason why equally good results cannot be obtained if both sides of the sheet are printed.

The base coat may comprise several types of preparations having a boiled linseed oil base or other suitable base which may be employed to produce a tacky surface. Many so-called lithographing varnishes may be employed. The pigments, of course, may vary depending upon the specific final effect desired.

My invention is particularly concerned with the preparation and use of the luminescent material by dusting. In addition to sulphides, I may use any of the usual silicates, tungstates, or the like. As partial esters with which to coat the luminescent material, there are a great many choices. In general, all of the partial esters referred to in my copending application, Serial No. 447,932, filed June 22, 1942, may be used to advantage. I have obtained the best results with partial esters of glycerin and ricinoleic acid, the very best results, so far as my present experimental work is concerned, being obtained with glycerol mono-ricinoleate. Mono-olein has given very good results, mono-laurin has shown fair results and the lauric acid mono-ester of diethylene glycol has also proven of value. While monostearine has also been used to advantage, its action has not been so pronounced as that of the other specific materials named hereinabove. Any partial ester of a relatively high molecular weight mono-carboxylic acid and a polyhydric alcohol seems to improve the adherence of the luminescent powder to the base coat and decrease markedly the tendency of the powder to adhere to

the paper. It has, also, the effect of improving the resistance of the printed characters to weathering. Those skilled in the art may refer to my copending application for additional examples of polyhydric alcohols and monocarboxylic acids which may be employed to produce partial esters suitable for use in the practice of my invention. I wish to point out, however, that such polyhydric alcohols as those previously referred to, which include sugars and sugar alcohols partially esterified with aliphatic mono carboxylic acids with at least six carbon atoms, particularly the unsaturated aliphatic acids, result in the production of compounds highly suitable for use in the practice of my invention.

While my process may be carried on exactly in the manner pointed out in the examples given hereinabove, I find that there is an advantage in introducing into the prepared powdered luminescent material a relatively small proportion (e. g. approximately 0.1% to 1.0%) of tricalcium phosphate. A recommended percentage is 0.25% to 0.50%, depending upon the degree of sub-division of the powdered material and the proportion of partial ester incorporated therewith. I find that when a small amount of tricalcium phosphate is dispersed substantially uniformly throughout the prepared powdered luminescent material, the luminescent material not only sifts more readily and becomes applied more uniformly to the surface, but the characteristics of the finished product are actually improved; in short, the results are consistently and uniformly satisfactory.

By means of my invention I am able to produce a highly acceptable printed article which in daylight appears as any ordinary printed page, but which at night is highly luminescent when subjected to the action of ultra violet light. While my invention is particularly concerned with the use of luminescent materials which are luminescent but which have little or no after glow, I may, if desired, utilize my invention in the production of printed articles which are phosphorescent as contrasted with luminescent. While, in general, my invention will usually be practiced with paper as the material forming the printed surface, other materials than paper may be used and have been used by me with good results.

The article produced in accordance with my invention is shown in Fig. 3. It may have various forms, depending upon the purpose to which it is to be put. It is believed that the drawing, taken with the general discussion of the method hereinabove, makes unnecessary further extensive amplification. A sheet 10 of paper is first treated to apply a black surface thereto, as indicated in Fig. 1, and the black surface then has applied thereto a tacky ink-like material in the form of relatively indistinct but clearly outlined letters 11 (Fig. 2). Immediately after printing, the surface of the sheet 10 containing the tacky letters 11 is dusted with powdered luminescent material containing a partial ester of glycerin and ricinoleic acid and a trace of tricalcium phosphate in the manner disclosed hereinabove. A part of this powdered material adheres to the tacky printed portion of the surface to produce slightly raised letters 12. The portion of the powder which does not adhere is then shaken or brushed off to leave the final article shown in Fig. 3. The sheet shown is illustrative of a sheet taken from a pilot's instruction book, the general arrangement only being indicated.

I do not limit myself to any particular features of my invention except in so far as the claims hereof are limited.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. In that method of applying characters to a surface, said characters being visible in both daylight and ultra-violet light, which comprises printing on said surface with a base coat comprising a tacky sizing material, and dusting on said base coat, while still tacky, a powdered luminescent material, the step which comprises utilizing as the luminescent material a powdered luminescent material the individual particles of which are in the main coated with a chemical compound comprising a partial ester of a relatively high molecular weight monocarboxylic acid and a polyhydric alcohol.

2. In that method of applying characters to a surface, said characters being visible in both daylight and ultra-violet light, which comprises printing on said surface with a base coat comprising a tacky sizing material, and dusting on said base coat, while still tacky, a powdered luminescent material, the step which comprises utilizing as the luminescent material a powdered luminescent material the individual particles of which are in the main coated with a chemical compound comprising a relatively high molecular weight mono-carboxylic acid mono-ester of glycerine.

3. In that method of applying characters to a surface, said characters being visible in both daylight and ultra-violet light, which comprises printing on said surface with a base coat comprising a tacky sizing material, and dusting on said base coat, while still tacky, a powdered luminescent material, the step which comprises utilizing as the luminescent material a powdered luminescent material the individual particles of which are in the main coated with a chemical compound comprising a higher molecular weight fatty acid mono-ester of glycerine.

4. In that method of applying characters to a surface, said characters being visible in both daylight and ultra-violet light, which comprises printing on said surface with a base coat comprising a tacky sizing material, and dusting on said base coat, while still tacky, a powdered luminescent material, the step which comprises utilizing as the luminescent material a powdered luminescent material the individual particles of which are in the main coated with glycerol mono ricinoleate.

5. As a new article of manufacture, an article providing a surface, and printed characters thereon, the printed characters comprising a base coat and a powdered luminescent material adherent thereto, the luminescent material having intimately admixed and associated therewith a chemical compound comprising a partial ester of a relatively high molecular weight mono-carboxylic acid and a polyhydric alcohol.

6. As a new article of manufacture, a paper-like article providing a surface, and printed characters thereon, the printed characters comprising a base coat and a powdered luminescent material adherent thereto, the luminescent material having intimately admixed and associated therewith a chemical compound comprising a relatively high molecular weight mono-carboxylic acid mono-ester of glycerine.

7. As a new article of manufacture, a paper-like article providing a surface, and printed char-

acters thereon, the printed characters comprising a base coat and a powdered luminescent material adherent thereto, the individual particles of the luminescent material being, in the main, coated with glycerol mono-ricinoleate.

8. In that method of applying characters to a surface, said characters being visible in both daylight and ultra violet light, which comprises printing on said surface with a base coat comprising a tacky sizing material and dusting on said base coat, while still tacky, a powdered luminescent material, the step which comprises utilizing as the luminescent material a powdered luminescent material admixed with an effective amount, not substantially more than about 1%, of tricalcium phosphate, the individual particles of said powdered luminescent material being, in the main, coated with a relatively high molecular weight aliphatic monocarboxylic acid partial ester of an aliphatic polyhydric alcohol.

9. A luminescent material comprising a powdered luminescent material the individual particles of which are, in the main, coated with a chemical compound comprising a partial ester of a relatively high molecular weight monocarboxylic acid and a polyhydric alcohol.

10. A luminescent material comprising a powdered luminescent material the individual particles of which are, in the main, coated with a chemical compound comprising a higher molecular weight fatty acid mono-ester of glycerine.

11. A luminescent material comprising a powdered luminescent material the individual particles of which are, in the main, coated with a minor proportion of glycerol mono-ricinoleate.

12. A luminescent material comprising a powdered luminescent material the individual particles of which are, in the main, coated with a higher molecular weight fatty acid mono-ester of an aliphatic polyhydric alcohol, said luminescent material also including, in intimate admixture therewith, a small proportion of tricalcium phosphate.

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