

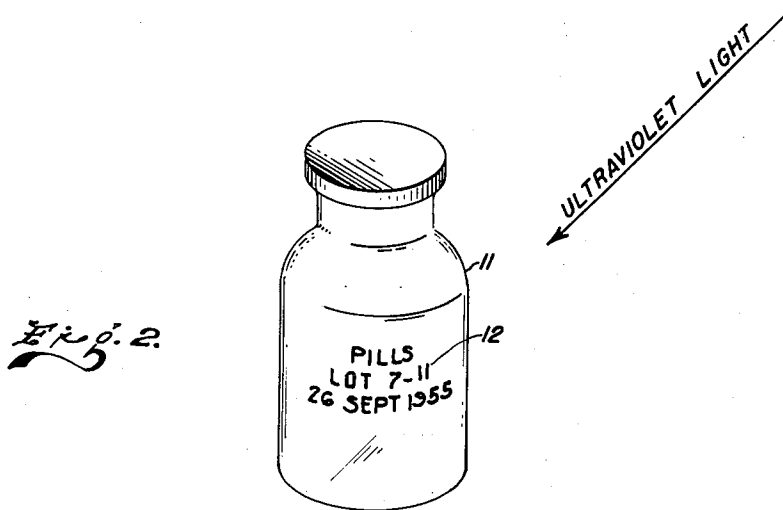
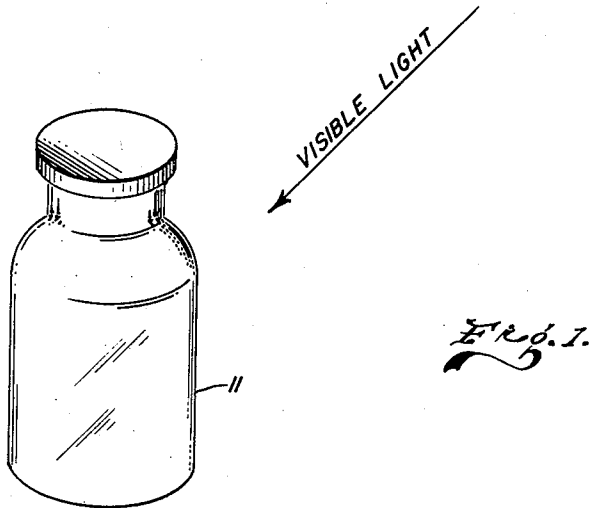
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FLUORESCENT GLASS CONTAINER MARKING

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2,929,931

FLUORESCENT GLASS CONTAINER MARKING

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3 Claims. (Cl. 250—71)

This invention relates to improvements in a method for marking glass containers, and the container so marked.

In certain manufacturing operations in which materials are placed in bottles or other glass containers, it is necessary or desirable that the container be permanently and unalterably marked for identification purposes but that the mark be of a nature which is easily concealed or is invisible to the casual observer. For example, foodstuffs may be packed in one factory but sold under various private brand labels.

Drugs may be packaged in a large production run, but the individual labelling may be done by the pharmacist in the corner drug store, or in any one of several languages for foreign distribution. It is thus necessary to identify the bottles so that there is no chance for error and yet have a marking which does not disconcert the casual observer.

Additionally, such markings serve to detect and prevent counterfeiting. In the drug trade, it is not uncommon for spurious items to be substituted for more valuable products. Invisible fluorescent markings serve to detect and prevent such substitution or "passing off" and enable a manufacturer to protect his product. By the choice of selected fluorescent compounds, in a proportion known only to the manufacturer, the detection of counterfeit products is greatly facilitated. Different ultra-violet light sources can give different responses depending on the fluorescent dyes selected.

Identifying compounds have been placed in various tablets to identify either the material or source, but such compounds mixed with the active ingredients are obviously undesirable contaminants.

Ultra-violet light fluorescing markings have been used in laundries as laundry marks to identify particular garments. Particles of dyes have been used in paper to detect counterfeiting. Such uses were limited to the identification of opaque objects.

In the past, bottles have been placed in boxes and the boxes marked, but the bottles may get in the wrong box, and testing before labelling is necessary in pharmaceutical practice. Temporary labels have been used, but these may accidentally fall off, or may require considerable costs in removal. Attempts have been made to code numbers in the glass, but such a method is very limited in flexibility.

We find that it is particularly convenient to mark glass containers with a transparent marking fluid which will be termed "ink" which fluoresces by ultra-violet light. By selecting a resin base for the ink which has an index of refraction which is nearly the same as that of the glass being marked, there may be obtained a mark on the surface of the glass container which is nearly invisible. By incorporating in this resin base a fluorescent dye, by ultra-violet light the coded marking clearly stands out for identification. By the same token, by normal illumination, the glass container has a marking which can only be discerned by getting a reflection from the

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surface of the glass at exactly the correct angle and which is nearly invisible even under these conditions. Such a marking is so nearly invisible that it would not be observed by casual inspection, particularly if a printed label is applied over the identification marking.

It is preferred that the composition of the matrix or base for the ink have an index of refraction close to that of the glass being marked. Among the suitable compositions for the base which may be used are the silicone resins, acrylic ester polymers, vinyl chloride polymers, polyvinyl alcohols, polyvinyl esters, butene polymers, lower alkyl celluloses, alkyl acrylate esters, and mixtures thereof. Drying oils such as linseed oil, or natural resins such as shellac may be used. The resins of the composition base may be used individually or in combination and the combination so adjusted that the index of refraction approaches that of the marked glass.

The index of refraction of the marked glass may vary over a considerable range. The index of refraction of bottle glass may vary from about 1.45 to 1.55—one particular lot of bottles had an index of refraction of 1.512. Special grades of glass vary above and below these limits. The index of refraction varies, of course, with the wavelength of the light being used for measurement and the temperature, but usually the D line of sodium at 25° C. is used, abbreviated as n_D^{25} .

The index of refraction of the resin is preferably selected so that in the polymerized final form on the glass, the index of refraction of the final composition approaches that of the glass. If the index of refraction of the composition is within about 0.1 of the glass, a transparent composition is not easily seen. If the index of refraction is within about 0.02 of the glass, the composition may be only distinguished by the most assiduous inspection. If the index of refraction of the composition cannot be conveniently matched to the glass the entire surface of the glass may be coated with the composition base and only selected portions with the fluorescent material, which gives the desired result. However, for purposes of economy and convenience, it is more economical to mark only selected areas and to use a composition which is substantially invisible. The composition should be applied in a sufficiently fluid condition for the surface to become smooth or "level" from surface tension.

Various types of fluorescent compounds may be used. Necessarily the fluorescent compound must be one which is invisible by ordinary light, which rules out any of the metallic compounds such as zinc sulfide. The newer "brighteners" are extremely active so that a very small amount of the fluorescent compound may be easily observed by ultra-violet light. The "brighteners" may be either soluble in the resin or, if insoluble in the resin, finely dispersed therein. The concentration depends upon the degree of fluorescence imparted by the fluorescent material, and the materials which fluoresce more brightly may be present in smaller quantities. Among the fluorescent compounds which are satisfactory are the 7-dialkylaminocoumarins such as for example 4-methyl-7-dimethylaminocoumarin, 4-methyl-7-diethylaminocoumarin and 4-ethyl-7-diethylaminocoumarin, Rhodamine B (color index 749) which is 6-diethylamino-9-(2-carboxyphenyl)-isoxanthene-3-diethylammonium chlorides; and 4-(2-hydroxyethylamino)-N-butyl-naphthalimide as disclosed in U.S. Patent 2,415,373. Anthracene and some of the earlier identified fluorescent compounds may be used in slightly larger concentrations.

Incorporated with the fluorescent dyes may be materials which are not fluorescent compounds in their own right but which sensitize the fluorescent compounds so that they fluoresce more brightly. Among such materials are esculin, quinine sulfate and umbelliferone.

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The markings may be merely dots of a coded nature or may be a complete label with letters and figures so that when viewed by fluorescent light comparatively complex information may be clearly visible.

For purposes of illustration, the accompany drawings 5 show our invention.

Figure 1 is a view of a marked bottle by ordinary light. Figure 2 is a view of a marked bottle by ultra-violet light.

The bottle 11 has on the surface thereof a legend of a resin composition containing a fluorescent material 12. When viewed by ultra-violet light, the fluorescent material clearly stands out and is easily read.

As illustrative of the material which may be used for marking, bottles of ordinary crown glass having an index of refraction of 1.512 were marked by printing, using rubber type, with certain resin compositions containing fluorescent materials.

Example 1

50 grams of methyl methacrylate, sold under the name "Acryloid A-101" by Rohm and Haas and having an n_D^{25} of 1.51, were mixed with 75 milliliters of xylene, 15 milliliters of chloroform, 35 milliliters of 2-butoxyethanol, 15 milliliters of ethyl lactate, 35 milliliters of butyl acetate and 10 milliliters of diethyl phthalate. To this suspension was added 100 milligrams of 4-methyl-7-diethylaminocoumarin. Glass bottles containing a pharmaceutical preparation were marked, using rubber type, with this fluorescent composition. After permitting the resin solution to dry, the bottles were examined by ultra-violet light. The markings stood out clearly and distinctly and were easily discernible. When examined by ordinary light, either artificial or sunlight, the resin composition on the surface of the glass was substantially invisible and could only be ascertained by the most detailed inspection. Unless the person looking for markings knew that there were such markings, the markings would not have been observed. n_D^{25} for dried resin film including the dye was 1.53.

Example 2

A mixture was prepared of 100 milligrams of 4-methyl-7-diethylaminocoumarin, 200 milliliters of chloroform and 200 milliliters of a 60% solution of polymerized alkylhalosilanes in toluene sold by Dow as silicone Resin 804, n_D^{25} was 1.45-1.46. Again, when used to mark bottles and permitted to dry, the marking was nearly invisible in daylight but fluoresced with clearly visible markings. n_D^{25} for dried resin film including the dye was 1.47.

Example 3

Another suitable composition was formed by dissolving 80 milligrams of anthracene, 5 milligrams of umbelliferone, 5 milligrams of esculin and 5 milligrams of quinine sulfate in 15 milliliters of N-methylpyrrolidone, and then adding 200 milliliters of ethanol; 200 milliliters of silicone Resin 804 were then added. This marking composition on glass bottles again gave satisfactory fluorescent identification. For the dried coating n_D^{25} was 1.48.

Example 4

A marking resin was formed by dissolving 100 milligrams of Rhodamine B in 2½ milliliters of N-methylpyrrolidone, 50 milliliters of chloroform and 150 milliliters of silicone Resin 804. Satisfactory fluorescent identification on glass bottles was obtained with this composition. For the dried resin including the dye, n_D^{25} was 1.46.

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Example 5

100 milligrams of 4-(2-hydroxyethylamino)-N-butyl-naphthalimide were mixed with 150 milliliters of xylene, 50 milliliters of chloroform, 300 milliliters of silicone Resin 804 and 6 drops of Span 80. Span 80 is a well known wetting agent consisting of polyoxyethylene sorbitol. A good fluorescent marking was obtained. For the dried resin and dye, n_D^{25} was 1.45.

Example 6

200 milligrams of 4-methyl-7-dimethylaminocoumarin were mixed into 960 milliliters of a 40% aqueous dispersion of an acrylic ester polymer sold as Rhoplex WN-80, n_D^{25} was 1.43. This marking composition gave satisfactory fluorescent identification on glass bottles. For the dried resin and dye, n_D^{25} was 1.41.

Example 7

100 milligrams of Rhodamine B Stearate were dissolved in 200 milliliters of toluene to which was then added 100 grams of a 60% solid mixture of polymers of normal and branched chain butenes sold as Oronite No. 24, n_D^{25} was 1.45. Bottles marked with this compound were dried by infra-red radiation and proved to have a satisfactory fluorescent identification. The dried resin including the dye, n_D^{25} was between 1.47 and 1.48.

Example 8

10 grams of ethyl cellulose, n_D^{25} was between 1.59 and 1.60, were dissolved in 160 milliliters of toluene and 40 milliliters of ethanol. As soon as a smooth solution was obtained, 100 milligrams of 4-methyl-7-dimethylaminocoumarin and 5 milliliters of dioctylphthalate were added. Legends on bottles marked with this composition were easily read under ultra-violet light. For the dried cellulose and dye, n_D^{25} was between 1.61 and 1.62.

Other compositions will readily suggest themselves to those skilled in the use of fluorescent materials.

The selection of the resin may be largely empirical but is easiest to determine by tests against the particular glass being used. Resins having a highly alicyclic character tend to have a higher index of refraction than basically aliphatic resins, and a mixture of the two to modify the index of refraction is frequently convenient.

The closer the index of refraction of the composition to that of the glass, the more nearly invisible the marking tends to be by normal illumination.

We claim:

1. A transparent glass container, contents therein to be identified, and on a smooth transparent glass surface thereof, a thin indicia of a visible-light invisible, visible-light transparent, fluorescent-light visible composition, comprising a fluorescent material dispersed in visible-light invisible form in a solvent soluble polymer, which polymer in the solid phase has an index of refraction within about 0.02 of the index of refraction of the container glass.

2. The container of claim 1 in which the air contacting surface of the composition has a smooth, flowed texture.

3. A glass container, contents therein to be identified, and on a smooth transparent glass surface thereof, a thin indicia of a visible-light invisible, fluorescent-light visible composition, comprising a fluorescent material dispersed in a solvent soluble polymer which in the solid phase has an index of refraction approximately equal to the index of refraction of the glass of the container, said indicia not being otherwise readily sensible.

(References on following page)

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References Cited in the file of this patent

UNITED STATES PATENTS

Re 22,530	Sell	Aug. 15, 1944	
1,032,610	Kern	July 16, 1912	
1,201,322	McCoach	Oct. 17, 1916	5
1,302,353	Friedrich	Apr. 29, 1919	
1,349,396	Van Clief	Aug. 10, 1920	
2,262,492	Farrell	Nov. 11, 1941	

2,306,939
2,318,089
2,382,806
2,527,043
2,566,713
2,594,903
2,756,344
2,763,785

6

Ferris	Dec. 29, 1942
Mattin	May 4, 1945
Motson	Aug. 14, 1945
Wallhausen	Oct. 24, 1950
Zworykin	Sept. 4, 1951
Freedman et al.	Apr. 29, 1952
Ferrier	July 24, 1956
Switzer	Sept. 18, 1956

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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Ferdinand Joseph Richter et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 48, for "Ulrrta-violet" read -- Ultra-violet --; column 3, line 5, for "accompany" read -- accompanying --; column 4, line 14, for "Rhoples" read -- Rhoplex --.

Signed and sealed this 20th day of September 1960.

(SEAL)

Attest:

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Commissioner of Patents