United States Patent

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[15] **3,639,762**

[45] **Feb. 1, 1972**

[54] MARKING CONSUMER ITEMS BY RENDERING COLORLESS MARKINGS PERMANENTLY COLORED WITH RADIATION EXPOSURE

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[22] Filed: **Feb. 14, 1969**

[21] Appl. No.: **801,244**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 563,340, July 1, 1966, abandoned.

[52] **U.S. Cl.** **250/71,** 250/65

[51] **Int. Cl.** **B44d 1/50**

[58] **Field of Search** 250/65.1, 71

[56] **References Cited**

UNITED STATES PATENTS

3,392,501 7/1968 Gilchrist, Jr. ..... 250/65.1 X

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[57] **ABSTRACT**

Consumer items are marked with two or more colorless markings each of which can be rendered colored by exposure to different levels of radiation. Exposure to one level of radiation selectively changes one marking to a substantially permanently colored, visible state without affecting the colorless state of the other markings.

9 Claims, 3 Drawing Figures

Fig. 2.

Fig. 1.

Fig. 3.

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MARKING CONSUMER ITEMS BY RENDERING COLORLESS MARKINGS PERMANENTLY COLORED WITH RADIATION EXPOSURE

This application is a continuation-in-part of my copending application Ser. No. 563,340, filed July 1, 1966 and now abandoned.

BACKGROUND

This invention relates to a method and apparatus for marking consumer items and to the items so marked. More specifically, this invention relates to method and apparatus for the high-speed, efficient marking of a plurality of consumer items such as can goods, boxes, overwrapped packages and the like.

Nowadays consumer items are mass produced in enormous quantities and marketed throughout the country to thousands of retail outlets. For instance, canned foods alone run to 40 billion units annually. Someone, usually the retailer, is faced with marking such items for price and the like. Some prepricing by the manufacturer is done but this limits the freedom of the retailer with respect to price options and discounts. The great bulk of marking, therefore, is done by the retailer. Almost without exception, marking at the consumer level is carried out by error prone hand stamping methods. In the first place, hand marking is a menial yet necessary and costly operation. Marking errors are replete because of hasty referral to the pricebook, inaccurate reading of previously marked items, faulty memory or just plain laziness on the part of the stock clerk. Obviously, marking errors erode profits and create unhappy customers.

Present day hand stamping methods more often than not result in illegible markings even if the correct marking is placed on the item. Illegible markings require a checker to inquire as to the correct price or results in his ringing up the price he thinks it says. This leads to lost time, increased costs, decreased profits, and unhappy customers who are not sure when they are being charged with the wrong price.

The present invention overcomes the problems heretofore met with hand stamping methods, and instead, provides an automatic or semiautomatic means for simultaneously marking a plurality of consumer items.

SUMMARY

Broadly the process of the present invention for marking consumer items comprises placing at least two different, normally colorless or invisible markings on a consumer item, the markings being unaffected by ambient light conditions but being capable of being rendered substantially permanently colored or visible to the naked eye by exposure to different levels of radiation or combinations thereof and selectively rendering one of the markings substantially permanently colored by exposing the marking to that level of radiation or combination of levels which will render the marking substantially permanently colored without affecting the normally colorless state of the other markings.

The consumer item produced in accordance with this invention has at least two different normally colorless markings thereon the markings being unaffected by ambient light conditions but being capable of being rendered substantially permanently colored by exposure of different levels of radiation, one of the markings being substantially permanently colored by virtue of having been exposed to that level of radiation that will render the marking colored without affecting the normally colorless state of the other markings.

Apparatus suitable for carrying out the method of this invention comprises means for advancing consumer items bearing a plurality of normally colorless markings to a marking station, selective radiation means adjacent the station comprising an activating station and means for activating the radiation means to a level of radiation such that one of the markings will be rendered colored by exposure thereto without affecting the normally colorless state of the other markings.

In the Drawings:

FIG. 1 illustrates consumer items bearing invisible markings which are shown in phantom.

FIG. 2 illustrates consumer items wherein one of the invisible markings has been rendered visible in accordance with the present invention.

FIG. 3 illustrates apparatus suitable for use in the present invention.

DESCRIPTION

The types of markings that may be employed in this invention include numbers for pricing or coding (such as universal item codings), symbols, letters for coding or to convey a message to the consumer, or to indicate quantity or quality, and the like. At least two or more markings are employed. The retailer is provided with a schedule of the normally colorless markings on the items from which he selects the marking he desires and renders it colored as is described in more detail below. The schedule of markings may appear on the case for case goods such as canned foods and the like or may be supplied separately to the retailer. The markings may be originally placed on the consumer items by the manufacturer of the items or by the manufacturer of the packages for the items or by some intermediate jobber.

Consumer items that can bear normally colorless markings in accordance with the present invention have sufficient space to accommodate the markings and include can goods, boxes, overwrapped packages, bulk items such as tools and the like, books, magazines, blister and skin packaged items, card mounted items and the like. The present invention is especially suited to marking case packed dry goods as are used in supermarkets such as canned foods, overwrapped packages, boxed dry foods, dairy items and the like.

As used herein, the phrase "ambient light conditions" is meant to include normal indoor lighting such as incandescent or fluorescent lighting and daylight. The phrase "substantially permanently colored or visible" is intended to describe a normally colorless marking rendered colored for a period of time at least equal to the span of time beginning when the marking is first rendered colored until the consumer item so marked is used and the container discarded by the consumer.

Electromagnetic radiations outside the visible spectrum can be employed in this invention. X-rays ultraviolet (UV) radiations and infrared (IR) radiations are three sources of suitable radiations and different levels within each type of these radiations may be used successfully in this invention. X-rays generally have wavelengths of from about 0.1 to about 100 Angstrom units (A.), UV radiations have wavelengths of less than about 4,000 A., generally from about 130 to about 4,000 A., and IR radiations have wavelengths of greater than 7,700 A. The visible spectrum ranges from about 4,000 to about 7,700 A. and the limit of the sun's UV on the surface of the earth is about 3,000 A. although in normal handling consumer items are rarely exposed to strong sunlight so that the practical effect of UV from the sun is very limited. Markings sensitive to UV wavelengths of up to 4,000 A., and preferably up to about 3,000 A. can be employed in this invention. X-rays are generated by cathode-ray tubes, UV by a carbon arc, sunlamps, electronic flash guns, germicidal lamps, mercury vapor lamps, tungsten arc lamps, and Kromeyer lamps and the like, and IR by a hot nonincandescent body and the like.

UV and IR radiations can be narrowed down to different selected bands of radiation thru the use of filters as is well known in the art. See, for example, Summer, W., *Ultra-Violet and Infra-Red Engineering*, Sir Isaac Pitman & Sons, Ltd., (London, 1962) pp. 53–74. Thru the proper use of filters, narrow bands UV and IR radiations can be chosen to render colored a normally colorless marking sensitive to the chosen narrow band of UV or IR radiation without affecting the normally colorless state of the other marking or markings. A suitable UV and IR filter is described in U.S. Pat. No. 2,881,663. Specific UV filters are described in the following U.S. Pat. Nos.: 2,816,047, 2,974,226, 3,015,253, 3,334,217, and 3,370,965. Specific IR filters are described in the following U.S. Pat. Nos.: 2,418,605, 2,813,802, 2,986,527, 3,051,596, 3,062,103 and 3,209,641.

Compounds and compositions useful in the present invention that are normally colorless and unaffected by ambient light conditions but are capable of being rendered colored by exposure to different levels of radiation are numerous and well known in the art.

A suitable normally colorless marking composition sensitive to UV is a leucocyanide of a triarylmethane dye dissolved in at least one carboxylic acid which transmits UV radiations of 2,100 to 4,000 A. as is disclosed in U.S. Pat. No. 2,528,496 issued Nov. 7, 1950. The use of certain carboxylic acids can narrow the range of UV sensitivity of these compositions. For example, aesculin confines UV sensitivity to 2,600–2,750 A. and greater than about 3,700 A.

Another normally colorless composition sensitive to UV radiations is the combination of a collageuous protein and a triprimaryamino-triphenylacetonitrile as is disclosed in U.S. Pat. No. 2,829,052, issued Apr. 1, 1958. An aqueous ammonia solution containing aurin cyanide dissolved therein, as disclosed in U.S. Pat. No. 2,855,304, issued Oct. 7, 1958, provides a normally colorless composition that possesses the relatively insensitivity to sunlight of the aurin cyanide free phenol.

Other suitable UV and shorter wavelength sensitive colorless marking compositions that are not sensitive to light in the visible range include: a combination of a hydrocolloid and a hydrophilic triphenylacetonitrile compound having at least one radical selected from the group of hydroxy and amino radicals in a position para to the central methane carbon atoms as disclosed in U.S. Pat. No. 2,855,303, issued Oct. 7, 1958; para-amino triphenylmethane dye cyanides having in the molecule at least one hydrophilic group as disclosed in U.S. Pat. No. 2,864,753, issued Dec. 16, 1958; and a hydrophilic cyanide of p-amino triphenylmethane dye having at least one hydroxy lower alkyl radical attached to the nitrogen atom of a p-amino group as disclosed in U.S. Pat. No. 2,877,169, issued Mar. 10, 1958.

Other suitable normally colorless marking compositions sensitive to UV radiations and shorter radiations such as X-rays include: a leucocyanide of a triphenylmethane dye and a cyanuric acid activator as disclosed in U.S. Pat. No. 3,079,258, issued Feb. 26, 1963; a leucocyanide of a triphenylmethane dye and boron containing compounds as activators as disclosed in U.S. Pat. No. 3,121,012, issued Feb. 11, 1964; a leucocyanide of a triphenylmethane dye and a titanium ester of an alkylene polyamine activator as disclosed in U.S. Pat. No. 3,131,062, issued Apr. 28, 1964; a colorless quaternary ammonium triphenylmethane carbinol and an alkoxyboroxine as disclosed in U.S. Pat. No. 3,123,473, issued Mar. 3, 1964; a chelated leucocyanide dye as disclosed in U.S. Pat. No. 3,184,308 issued May 18, 1965; and a leucocyanide of a naphthyl methane dye and a strongly acid nonoxidizing activator as disclosed in U.S. Pat. No. 3,205,072, issued Sept. 7, 1965.

The leucocyanide dyes described in the aforementioned patents vary in their sensitivity with different wavelengths. In general, the range of wavelengths in which sensitivity mainly occurs is approximately 2,000 to 4,000 A. with strongest sensitivity lying in the range of 2,500 to 3,400 A. Thus it is possible to select as markings for use in this invention, normally colorless leucocyanide dyes, as well as other normally colorless compounds and compositions such as those disclosed in the aforementioned patents, that are sensitive to different levels of radiation lower than about 4,000 A. For example, a leucocyanide solution containing aesculin (as described in said U.S. Pat. No. 2,528,496) is sensitive to UV radiations of 2,600–2,750 A., whereas a hydrocolloid and a hydrophilic triphenylacetonitrile compound (as described in said U.S. Pat. No. 2,855,303) is sensitive to UV radiations shorter than 3,350 A., and leucocyanide dyes in conjunction with an inorganic metallic salt phosphor and an activator, as described in U.S. Pat. No. 3,226,233, issued Dec. 28, 1965, is sensitive to UV radiations of 2,500 to 2,600 A. since the phosphor when exposed to such radiations, emit radiations in the range of 3,000 to 3,400 A. to which the leucocyanide is sensitive.

Another suitable normally colorless marking composition sensitive to UV radiations but stable under sunlight, fluorescent or incandescent light is a leucocyanide dye and 2-methyl-4,5,6,7-tetrachlorobenzotriazole as disclosed in U.S. Pat. No. 2,927,025, issued Mar. 1, 1960. Still another leucocyanide dye compositions are disclosed in U.S. Pat. No. 3,121,632, issued Feb. 18, 1964.

Another class of compositions are heat or IR sensitive such as those described in U.S. Pat. No. 3,238,047, Mar. 1, 1966, wherein the formation of colored inorganic pigments, such as metal sulfides, is disclosed.

Two or more normally colorless markings sensitive to different levels of IR can be used in this invention. For example, one colorless marking can be sensitive to 8,000 A. (in the infrared) and another to 9,000 A. Exposure of these markings to 8,000 A. would render the first marking colored without affecting the normally colorless state of the second marking. Exposure to 9,000 A. would render the second marking colored without affecting the normally colorless state of the first marking.

U.S. Pat. No. 3,116,148, issued Dec. 31, 1963, discloses normally colorless compositions that can be rendered colored upon exposure to IR and UV radiations but are insensitive to UV radiation alone. The normally colorless marking is a profuse interspersion of solid particles of substantially colorless organic dye former material which is sensitive to UV radiations when in solution and heat-rupturable capsules containing a liquid solvent for the dye material. Exposure of the marking to heat radiation produces a gas in the capsules rupturing same and releasing a liquid solvent for the dye. Subsequent or simultaneous exposure to UV radiation renders the marking colored. Exposure to UV alone without rupturing the capsules does not change the normally colorless state of the marking. Another system sensitive to UV and IR is described in U.S. Pat. No. 3,236,648, issued Feb. 22, 1966. In this patent a dye cyanide and a thermally fusible activator therefor (such as carboxylic acid amides, phosphonic acid esters, carboxylic acids, amines, polyoxy compounds, nitriles, aromatic carbinols and the like) are mixed together to produce a colorless marking. Exposure to IR (heat) above the fusion point of the activator meets same and exposure to UV while the activator is in the liquid state changes the dye cyanide to the colored state. Exposure to UV alone does not affect the normally colorless state of the marking. Thus, it should be noted that the phrase " exposure to different levels of radiation" is intended to include a combination of radiations (such as UV and IR) which will render a marking colored without affecting the normally colorless state of another marking sensitive, for example, to one level of UV different from the level of UV used in combination with IR.

A UV sensitive marking is described in U.S. Pat. No. 3,285,743 and comprises a colorless leucocyanide dye adapted to be rendered colored upon exposure of up to 3,600 A. and an organic heterocyclic compound which generates a bifunctional coupling intermediate upon exposure of up to 3,600 A. The coupling intermediate and dye combine upon exposure of up to 3,600 A. to form a colored marking.

Normally colorless leuco dye markings capable of being rendered permanently colored upon exposure to 2,000–4,200 A. are described in U.S. Pat. No. 3,359,109, issued Dec. 19, 1967 (in combination with an N,N,O-tri-acylhydroxylamine); in U.S. Pat. No. 3,360,370, issued Dec. 26, 1967 (in combination with an aromatic ditriazole); and in U.S. Pat. No. 3,364,030, issued Jan. 16, 1968 (in combination with a diacylazino compound).

Another normally colorless marking sensitive to UV in the range of 2,000–4,200 A. comprises a triphenylmethane derivative and a nonvolatile nitrogen-containing photooxidant as described in U.S. Pat. No. 3,390,997, issued July 2, 1968.

Other normally colorless markings are marketed under the trademark "Dylux" by E. I. duPont de Nemours and Company. These normally colorless markings are sensitive to UV or heat (IR) and have the unique feature of being capable of

being rendered colored upon exposure to a given level of UV or heat (IR) and can also be rendered completely insensitive (or deactivated) upon exposure to a different level of UV or ambient light. Thus, two or more of these markings can be used, one rendered colored by exposure to a given level of UV or heat (IR) and the others deactivated or rendered permanently colorless upon exposure to a different level of UV or ambient light. One such system is described in U.S. Pat. No. 3,390,996, issued July 2, 1968, and comprises a leuco dye, a photo-oxidant which upon UV irradiation oxidizes the leuco dye, and a redox couple which when activated by light (different level of radiation than that which causes oxidation of the leuco dye) reacts with the photo-oxidant to deactivate it. A similar system is described in U.S. Pat. No. 3,390,994, issued July 2, 1968, and comprises an acid salt of a leuco aminotriarylmethane, a hexaarylbiimidazole (photo-oxidant) and a redox couple.

Two normally colorless systems capable of being rendered colored and deactivated (permanently colorless) use combinations of UV and heat (IR). One (the first) system uses heat (IR) to color and UV to deactivate is disclosed in U.S. Pat. No. 3,383,212, issued May 14, 1968, and comprises a leuco dye, a thermally activatable oxidant for the dye and a redox couple which upon exposure to UV reacts with the oxidant to deactivate it. The (second) reverse system, using UV to color and heat (IR) to deactivate, is described in U.S. Pat. No. 3,390,995, issued July 2, 1968, and comprises a leuco dye, a photo-oxidant for the dye and an organic compound capable of forming a reducing agent upon exposure to heat (IR) which will react with the photo-oxidant deactivating it. Thus, these two normally colorless systems can be readily used in this invention. One marking from the first system and a second marking from the second system can both be placed on a consumer item such as a can in a colorless state. Exposure to heat (IR) renders the marking from the first system colored and deactivates (renders permanently colorless) the marking from the second system. If the opposite result is desired, exposure to UV renders the marking from the second system colored and deactivates the marking from the first system.

The aforementioned patents are incorporated herein by reference.

Suitable apparatus for use in this invention includes conveyor or hand operated stationing means to bring the consumer items into a marking position. A source of IR radiation and several sources of different levels of UV radiation and/or X-rays are conveniently mounted to expose the markings on the consumer items. Various combinations of moveable filters can also be conveniently mounted below the sources of radiation. The stock clerk at the retail outlet selects the desired marking from the schedule on the packing case or box or from any otherwise furnished schedule selects the proper filter if one is needed and activates and exposes the marked surface of the consumer item to that source of radiation which will convert the desired marking to the colored state without affecting the colorless state of the other markings that may be there. A scaning device can also be employed to automatically "read" and select a predesignated marking.

Thus, the present invention can be used to automatically or semiautomatically mark a plurality of consumer items on a continuous or semicontinuous basis.

By way of example in reference to the drawing, a plurality of cases of canned food goods **10** are marked on the top by the canner with the colorless markings, 15¢ and 2/29¢ (shown in phantom in FIG. 1). The first marking **12** is applied from a colorless solution of victoria blue leucocyanide, a solvent and aesculin (as described in said U.S. Pat. No. 2,528,494) which is sensitive to UV radiations of about 2,600–2,750 A. The second marking **14** is applied from a colorless solution of leucocyanide of crystal violet, resorcinol dimethyl ether, cellulose acetatebutrate in toluene and ethyl acetate, dioxane and a tungstate type phosphor (as described in said U.S. Pat. No. 3,226,233) which is sensitive to UV radiations of the order of 2,537 A. The nature of the colorless markings is indicated on the outside of the boxes **16** in which the canned goods are packed and shipped (FIG. 3). At the retail outlet, a marking station (FIG. 3) is provided with a source of UV light **18** of the order of 2,537 A. and a source of UV light **20** of the order of 2,600–2,750 A. (not shown) with means to activate each source. The retail clerk selects the second marking **14**, activates the 2,537 A. UV light source **20** and passes the opened cases thru the activating station and under the UV light source **20** (FIG. 3). The result is that each can bears a clearly visible, substantially permanent and sharp marking (2/29 ¢) while the other marking (15¢) remains in the colorless state and is not visible to the consumer (FIG. 2).

It is also within the scope of the present invention to place two or more colored markings on a consumer item each of which can be selectively rendered colorless by exposure to different levels of radiation such as UV or IR, with or without the use of suitable filters, as described herein. This approach has the advantage of enabling the retailer to readily see the markings available to him and to render colorless the markings he desires not to use while maintaining the marking he has chosen in the colored, visible state.

I claim:

1. Process for marking consumer items which comprises placing at least two different, normally colorless markings on a consumer item, said markings being unaffected by ambient light conditions but being capable of being rendered substantially permanently colored by exposure to different levels of radiation, and selectively rendering one of said markings substantially permanently colored by exposing said marking to that level of radiation that will render said marking colored without affecting the normally colorless state of the other markings.

2. Process of claim **1** wherein a plurality of consumer items are marked simultaneously.

3. Process of claim **1** wherein one marking is sensitive to infrared and deactivated by being rendered permanently colorless, by ultraviolet and a second marking is sensitive to ultraviolet and deactivated by infrared.

4. Consumer item having at least two different, normally colorless markings thereon, said marking being unaffected by ambient light conditions but being capable of being rendered substantially permanently colored by exposure to different levels of radiation, one of said markings being substantially permanently colored by virtue of having been exposed to that level of radiation that will render said marking colored without affecting the normally colorless state of the other markings.

5. Consumer item of claim **4** wherein said markings are sensitive to different levels of ultraviolet and/or infrared radiations.

6. Consumer item of claim **4** wherein one marking is sensitive to infrared and deactivated by being rendered permanently colorless by ultraviolet and a second marking is sensitive to ultraviolet and deactivated by infrared.

7. Apparatus for marking consumer items having at least two normally colorless markings thereon, said markings being capable of being rendered substantially permanently colored by exposure to different levels of radiation, which comprises means for advancing said consumer item to a marking station, selective radiation means adjacent said station comprising an activating station and means for activating said radiation means to a level of radiation such that one of said markings will be rendered colored by exposure thereto without affecting the normally colorless state of the other markings.

8. Apparatus of claim **7** wherein said radiation means comprises sources of ultraviolet and infrared radiations.

9. Apparatus of claim **7** wherein said radiation means include filter means.

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