

1

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STERILIZATION INDICATOR COATING

Constantine Carumpalos, Mountainside, N.J., assignor to
United States Envelope Company, Springfield, Mass.,
a corporation of Maine
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This invention relates in general to the preparation of matter for visually indicating whether or not that matter has been subjected to sterilization conditions. More particularly, the invention relates to the preparation of articles, usually of paper or similar material, by the application thereto of a particular kind of coating preferably in the form of an ink, which changes from one distinct color to another when the article on which it is applied is subjected to sterilization conditions, to indicate that sterilization conditions have been attained.

This invention is especially applicable in the sterilization of medical instruments, formula-containing baby bottles, or the like, at hospitals. For instance, the need for adequate control measures in infant feeding to reduce the death rate of new-borns is recognized as a basic challenge to hospitals throughout the world. Among the known preventable causes of death in infants, infections are recognized as being one of the most important. It has become the practice in a good many hospitals to apply disposable protective caps to formula-containing bottles before they are sterilized. The bottles and caps are thus sterilized together, and the caps remain on the bottles until they are ready for use to prevent contamination subsequent to sterilization.

In such sterilization procedures, it is necessary that the bottles which have been completely sterilized be capable of ready identification. It is necessary to be able to visually identify bottles which have been sterilized, as distinguished from unsterilized bottles in the event of accidental intermingling of bottles, some, but not all of which have been sterilized.

It is an object of this invention to provide the articles with a coating which will change from one distinct color to another only when sterilization conditions have been attained.

It is a further object of this invention to provide a coating for articles which are to be sterilized, which may be printed as an ink onto such articles, and which is resistant to premature color changes in storage under adverse-temperature and humidity conditions.

Other objects will appear hereinafter. The ultimate objective of the invention, of course, is to reduce the number of infections in hospitals by using only articles which are absolutely sterile.

In the manufacture of paper caps for baby-formula containing bottles, for example, there are certain requirements which must be met by the indicator coating before it will be acceptable. In the manufacture of such caps, it is desirable to print words, strips, or other markings in such a manner that a change in color thereof will be readily visible. The paper caps are very often stored for long periods of time, possibly six months or even longer, before use. In certain parts of the country where warm and humid weather conditions exist, the indicator coating on the paper caps must resist premature color changes. If a premature color change occurs, then the entire stock may become useless, or even worse, if the premature color change goes unnoticed, a false indication of sterilization may exist on non-sterile articles. This, needless to say, may bring about serious results.

Furthermore, the color-changing sterilization indicator should be a liquid capable of being applied to the articles which are to be sterilized by ordinary printing machinery. Paper caps for baby formula bottles are manufactured by

2

the millions, and the only feasible way of applying the indicator coating is by a printing process. The coating must not be adversely affected, as by noticeable fading or running, by the moisture in steam sterilization.

The coating composition used in the present invention basically possesses the physical characteristics of an ink. The various ingredients are held together in a binder, the composition being of such a viscosity that it is adapted for printing with ordinary printing machinery. The color changing feature of the composition is provided by the incorporation therein of a leuco ester of a vat dye which is capable of being printed in its undeveloped vat color. The use of a single dye ingredient in a sterilization indicator coating such as this is highly desirable because both the undeveloped and developed color of the coating composition are easily controlled. Furthermore, it does not possess the undesirable feature of changing color with age which is found in some of the multi-dye indicating systems.

It has been found that by incorporating into the composition certain oxidizing and acid splitting agents, the vat color of the dye will develop simultaneously as the article or material, on which the dye is coated, is sterilized. When the coated article has been completely sterilized, the color of the dye has completely developed. The dye in the composition is retained in its undeveloped state previous to sterilization with the aid of an alkali and an amine, which are held in the coating by a binder. It is preferred to use ammonium hydroxide and a mono-valent tertiary amine. During steam sterilization of the articles onto which this coating composition is applied, the acid splitting agent liberates an acid, and along with the oxidizing agent, provides an acid oxidizing medium which causes regeneration of the vat dye by oxidizing the dye in the presence of an acid medium. The acid splitting agent is sufficiently strong to lower the pH of the coating from a pH well above neutral down to 5 or below.

With the use of certain leuco esters of indigoid type vat dyes, it is possible to start with a coating composition which is colorless, or one which has a pale yellow color, and develop a strong, distinct color. With the use of certain leuco esters of anthraquinonoid type dyes, a muddy brown, maroon, or red color will develop into a bright blue, green or orange color. In some cases, both the undeveloped and developed colors are important. For instance, it has been found to be desirable to have a coating which appears red before sterilization, and green afterwards, obviously in conformity with the "stop" and "go" signals.

While the ammonium hydroxide was incorporated into the composition specifically for preventing premature color change, the resulting coating was found to be acceptable only in certain climates, because heat and high humidity conditions would cause premature color change even though the ammonium hydroxide held the pH of the composition above seven. The mono-valent tertiary amine was incorporated into the composition for the purpose of improving printability characteristics. The addition of the mono-valent tertiary amine had the surprising effect of preventing premature color change of the coating even in warm and humid climates.

A variety of dyes, acid splitting agents, and oxidizing agents may be used in the coating composition according to this invention. It is preferred to use an anthraquinonoid type vat dye. Generally this type of dye provides a distinct color change as well as having very desirable colors.

Some of the acid splitting agents found to be effective in the coating composition are as follows: tetraethanol, ammonium hydroxide, ammonium sulphate, ammonium oxalate, ammonium thiocyanate, ammonium gluconate, and ammonium metavanadate. The oxidizing agent may

3

be, for example, sodium chlorate. The binder is preferably a resinous type binder such as polyvinyl alcohol, and must be of a viscosity such as to result in a coating composition of printable viscosity. It should also be water soluble before printing, but water resistant after printing to prevent undue fading or fanning of the coating when subjected to steam sterilization conditions.

The mono-valent, tertiary amine is characterized as an "invert soap" having colloidal properties. Furthermore, being cationic in nature, it forms a complex which imparts water resistance to polyvinyl alcohol. Without addition of the amine, the polyvinyl alcohol would not become insoluble in water before sterilization. The polyvinyl alcohol must be water soluble at the time the coating composition is made up, but it is highly desirable that it be water insoluble before sterilization to prevent bleeding of the dye.

Ordinarily the amine, being cationic in nature, is incompatible with the dye. Therefore, they must be held together in a colloidal suspension. The protective colloid is a partially hydrolyzed grade of polyvinyl alcohol which is an effective emulsifying agent, and also may have a viscosity low enough for use in inks.

In the examples which follow, Algosol Olive Green IB (CF), Algosol Golden Yellow IRK, and Algosol Blue IBC are leuco esters of anthraquinonoid type vat dyes manufactured by General Aniline and Film Corporation, and identified in the 1954 Technical Manual and Year Book of the American Association of Textile Chemists and Colorists. Gelvatol 40-10 is a partially hydrolyzed polyvinyl alcohol manufactured by Shawinigan Resins Corporation, and Amine O is a mono-valent tertiary amine manufactured by Geigy Chemical Company. The antifoam agent used was DC Antifoam A emulsion, a product of Dow-Corning Corporation. The percentages used are weight measures.

Also in the examples which follow, the catalyst comprised the following:

57.00 % water
8.70% of a 28% solution of ammonium hydroxide
17.15% ammonium gluconate
17.15% sodium chlorate

This catalyst contained the acid splitting and oxidizing agents, as well as the alkali for holding the pH of the composition up.

Example 1

Ingredients of composition:

	Percent
Polyvinyl alcohol binder, Gelvatol 40-10	20.00
Water	39.70
Dye, Algosol Olive Green IB (CF)	10.00
Catalyst	15.00
Anhydrous ethyl alcohol	15.00
Antifoam agent, DC Antifoam A emulsion	0.30

The polyvinyl alcohol was added to the cold water. This was heated to 150° F. while stirring, during which time the antifoam agent was added. When the polyvinyl alcohol had completely dissolved, the dye was added. After the dye had completely dissolved, the solution was cooled. The catalyst was added next, and while mixing, the alcohol was added as a solvent to aid in rendering the composition printable. This coating composition was then printed on paper articles, the coating having an initial color of maroon. When the articles were exposed to steam sterilization conditions until the articles had been completely sterilized, the coating turned a dark green color. The coating, however, was not sufficiently resistant to water, and had a tendency to run during steam sterilization. When the samples of paper coated with this composition were stored for an appreciable length of time under relatively high heat and relative humidity conditions, the coating displayed a tendency to change from its initial maroon color to a green color even

4

through it had not been subjected to sterilization conditions.

Example 2

Ingredients of composition:

	Percent
Polyvinyl alcohol binder, Gelvatol 40-10	20.00
Water	39.70
Antifoam agent, DC Antifoam A emulsion	.30
Dye, 5% Algosol Golden Yellow IRK-5%	
Algosol Blue IBC	10.00
Catalyst	15.00
Anhydrous ethyl alcohol	15.00

The polyvinyl alcohol was added to cold water. This mixture was heated to 150° F. while stirring, during which time the antifoam agent was added. When the polyvinyl alcohol was completely dissolved, the dyes were added. After the dyes had completely dissolved, the solution was cooled. The catalyst was added next, and while mixing, the alcohol was added as a solvent to aid in rendering the composition printable. The coating composition was then printed on paper articles. When the articles were exposed to steam sterilization conditions until the articles had been completely sterilized, there was no noticeable change in color of the coating because the developed color of the dyes was found to be the same as the undeveloped color. The samples were not subjected to storage tests to determine the effect of prolonged heat and high relative humidity, because of this composition's inability to change colors when the dyes were developed. Obviously, this composition would not be acceptable.

Example 3

Ingredients of composition:

	Percent
Polyvinyl alcohol binder, Gelvatol 40-10	20.00
Water	39.20
Antifoam agent, D.C. antifoam A emulsion	0.30
Dye, Algosol Olive Green IB (CF)	10.00
Catalyst	20.00
Anhydrous ethyl alcohol	10.00
Amine, Amine O	0.50

The polyvinyl alcohol was added to the cold water. The mixture was heated to 150° F. while stirring, during which time the anti-foam agent was added. When the polyvinyl alcohol was completely dissolved, the dye was added. After the dye had completely dissolved, the solution was cooled. The catalyst was added next, and while mixing, the alcohol was added as a solvent to aid in rendering the composition printable. The amine was added next. The coating was printed on a paper sample and subjected to steam sterilization conditions for a time sufficient to effect sterilization. The initial color of the coating was maroon, but the color after being subjected to sterilization was green. Like samples were also tested in storage under abnormally high heat and relative humidity conditions. The samples showed no tendency to change color prematurely under these adverse conditions. Printability on paper was very good.

I claim:

1. A composition for printing telltale insignia indicating, by a change in color, that sterilization conditions have been attained which comprises, by weight, approximately 20% partially hydrolyzed polyvinyl alcohol, approximately 40% water, approximately 10% of a leuco ester of an anthraquinonoid type vat dye, approximately 15% of a catalyst comprising an acid splitting agent, an oxidizing agent, and an alkali, approximately 15% anhydrous ethyl alcohol, an antifoam agent, and a mono-valent tertiary amine.

2. A composition according to claim 1 in which said catalyst comprises water, ammonium hydroxide, ammonium gluconate, and sodium chlorate.

5

3. A composition for printing telltale insignia indicating, by a change in color, that sterilization conditions have been attained which comprises, by weight, approximately 20% partially hydrolyzed polyvinyl alcohol, approximately 40% water, approximately 10% of a leuco ester of an indigoid type vat dye, approximately 15% of a catalyst comprising an acid splitting agent, an oxidizing agent, and an alkali, approximately 15% anhydrous ethyl alcohol, an antifoam agent and a mono-valent tertiary amine.

4. A composition according to claim 3 in which the catalyst comprises water, ammonium hydroxide, ammonium gluconate, and sodium chlorate.

5. A composition for printing telltale insignia indicating, by a change in color, that sterilization conditions have been attained which comprises, by weight approximately 20.00% partially hydrolyzed polyvinyl alcohol, approximately 50.60% water, approximately 0.30% antifoam agent, approximately 10.00% of a leuco ester of an anthraquinonoid type vat dye, approximately 10.00% anhydrous ethyl alcohol, approximately 0.50% of a mono-valent tertiary amine, approximately 1.74% of a 28% solution of ammonium hydroxide, approximately 3.43% of ammonium gluconate, and approximately 3.43% of sodium chlorate.

6. The method of preparing matter for changing color

6

when subjected to steam sterilization conditions which comprises the steps of

(a) preparing a coating which contains as its essential components, by weight, approximately 20.00% partially hydrolyzed polyvinyl alcohol, approximately 50.60% water, approximately 0.30% antifoam agent, approximately 10.00% of a leuco ester of an anthraquinonoid type vat dye, approximately 10.00% anhydrous ethyl alcohol, approximately 0.50% of a mono-valent tertiary amine, approximately 1.74% of a 28% solution of ammonium hydroxide, approximately 3.43% of ammonium gluconate, and approximately 3.43% of sodium chlorate, and

(b) applying the composition as a coating to the matter.

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MURRAY TILLMAN, *Primary Examiner*.

SAMUEL H. BLECH, *Examiner*.

W. J. BRIGGS, SR., *Assistant Examiner*.