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PHOTOGRAPHIC EMULSION FOR SPRAYING UPON SURFACES AND ITS APPLICATION

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This invention relates to photographic emulsions adapted for spraying upon surfaces consisting of a dispersion of silver halide in a solution of a far hydrolyzed cellulose ester in a solvent mixture consisting of water, a high boiling liquid and a low boiling solvent in proportions conducive to the application of emulsions to surfaces in this manner. This invention also relates to the process of applying light-sensitive emulsions to surfaces by spraying.

Light-sensitive photographic emulsions are usually employed by coating a thin layer of those emulsions onto a support of some type. For instance, for the ordinary variety of photographic film, the photographic emulsion is coated upon sheeting of a cellulose ester. For photographic paper, the paper serves as the support for a thin coating of emulsion thereon. At the present time, metal materials, particularly in the form of sheeting, are coated with photographic emulsions. It is to products of this nature that the spraying of emulsions is particularly adapted, as the coating can be applied quite rapidly thereto.

In the coating of metals, the forming of an oxide coating thereon, which is then impregnated with light-sensitive material, has been suggested. In some cases of this nature, special light conditions have been necessary to form an image thereon and the light-sensitive layer has not been readily susceptible to processing in the conventional manner. In some cases, the spraying of gelatin emulsions onto surfaces has been suggested. To our knowledge, in no case has the spraying of a gelatin emulsion onto a support been satisfactory, either the gelatin, which has been sprayed on, swelled and softened in processing or did not hold up in handling.

An object of this invention is to provide a process by which a satisfactory light-sensitive coating may be formed on a surface, particularly of metal. Another object of this invention is to provide photographic emulsions which are particularly adapted for this purpose. Other objects will appear herein.

We have found that emulsions of far hydrolyzed cellulose esters, using proportions of various types of liquids within certain limits, can be sprayed upon surfaces to form light-sensitive coatings of sufficient strength for that purpose and yet with satisfactory photographic properties. We have found that the photographic emulsions, as specified herein, when sprayed upon a surface have good spreading characteristics, form a smooth surface and may be dried very rapidly by a current of warm air. These emulsions, after exposure, can be readily processed by the usual methods employed in processing exposed photographic emulsions. These emulsions, after spraying onto a surface and exposing, are susceptible to rapid deevlopment in the conventional developing baths, rapid fixing in "hypo" solution and may be very rapidly dried after the processing treatment. The emulsion sprayed onto a surface in accordance with our invention, retains its hardness during the processing operation in contrast with the characteristics of gelatin emulsions which have been so applied.

The cellulose esters, which are suitable for use in our emulsions, are the far hydrolyzed, lower fatty acid esters of cellulose the preparation of these esters being described and claimed in Fordyce Patent No. 2,129,052. The cellulose esters, which we prefer to employ for this purpose are those which have been hydrolyzed down to an acyl content of 19–26%. For instance, a cellulose acetate propionate or a cellulose acetate, which has been hydrolyzed down to an acyl content, for example of 20%, 22% or 25% is suited for use in preparing an emulsion adapted for spraying in accordance with our invention. That these esters are suitable for preparing photographic emulsions is disclosed in U. S. Patent No. 2,110,491 of Salo. This patent, however, does not teach the conditions under which spray-coating of an emulsion can be accomplished nor does it teach the emulsion composition described herein. It is preferred that the ratio of the cellulose ester to the total solvents in the emulsion be between 1/30 and 1/50, although this range may be exceeded in emulsions using smaller proportions of silver halide than ordinarily employed, or where a low viscosity cellulose ester is used. By using a large proportion of silver halide or a high viscosity cellulose ester in preparing the photographic emulsion, an even smaller fraction of cellulose ester to total solvent than specified may be employed.

The emulsions in accordance with this invention consist primarily of a dispersion of silver halide in a solution of a far hydrolyzed cellulose ester, the solvent consisting of water, a critical proportion range of solvent boiling above 110° C. and the remainder of solvent boiling below 110° C. The emulsion may be prepared by first dissolving an alkali metal halide salt in a solution of the cellulose ester in an aqueous solvent. A solution of silver nitrate may then be mixed in to form a suspension of the silver halide in

the solution. By thorough stirring, the silver halide particles are dispersed throughout the solution. The emulsion may then be made up to the required composition or the acetate and the halide salt may be precipitated out and washed and then redissolved so as to be made up to the required composition. Obviously, other methods of preparing the emulsion may be employed. For instance, the silver halide may be first prepared in a dispersing agent, such as a water-soluble ethanolamine cellulose acetate and the emulsion may then be prepared by bringing it up to the proportions which are specified herein.

The silver halide portion of the emulsion may be either silver chloride, silver bromide or silver iodide, or preferably a mixture of these halides with silver bromide predominating. The liquid portion of the emulsion is made up of water, a water-miscible solvent boiling below 110° which when mixed with water will dissolve far hydrolyzed cellulose esters and a water miscible solvent boiling above 110°. The proportion of water in the solvent mixture should be within the range of 10–60% to provide an emulsion which has good spraying characteristics. The amount of water which is employed depends upon the feature which it is desired to emphasize. If the resulting product is to be subjected to rough usage, it is preferred that a limit of water in the lower half of the range be employed. If, however, the primary consideration is the photographic properties, a proportion of water in the upper half of the range given is desirable. The amount of water-miscible solvent, having a boiling point above 110°, which is employed in a photographic emulsion in accordance with this invention, should be in an amount within the range of 5–30% of the total solvent mixture. The solvent boiling above 110° C., if used in too great an amount, may affect the photographic properties of the emulsion. All of the remainder of the solvent mixture should be a water-miscible organic solvent boiling below 110° C., which solvent will dissolve the far hydrolyzed cellulose esters when mixed with water. Some of the water-miscible organic solvents, which boil below 110° C., which are suitable in emulsions in accordance with this invention, are acetone, methyl, ethyl, propyl or isopropyl alcohol, methyl ethyl ketone, ethylene formal, dioxane and methyl acetate. In some cases the solvent boiling below 110° C. may be made up of a mixture. For instance, ethyl acetate along with other solvents may dissolve a far hydrolyzed cellulose ester and, therefore, a mixture, such as ethyl acetate and ethyl alcohol may be employed in this capacity instead of the ethyl alcohol alone.

Water-miscible liquid solvents which boil above 110° C., which are suitable for use in emulsions in accordance with our invention, are butyl alcohol, amyl alcohol, glycols, such as ethylene glycol or glycerol, glycol mono- or diacetate, glycol monomethyl ether, methyl or ethyl cellosolve, cellosolve acetate, diethylene glycol, ethyl lactate and butyl lactate. The suitability of some solvents boiling above 110° C. depends upon the low boling solvent which is employed. For instance, cyclohexanone or butyl alcohol, although not soluble in water, may be soluble in various combinations of water and low boilers and hence are sufficiently water miscible to be employed in an emulsion in accordance with our invention. It is to be understood that the solvents used in emulsions of this invention shall be inert with respect to the other constituents thereof. It is also to be understood that the addition of sensitizing dyes, toning substances, ripeners, plasticizers, or the like, all as have been previously disclosed in the art, is permissible in the emulsions described herein. The emulsions of this invention are preferably plasticized by adding a small proportion (such as on the order of 1%) of a material such as monoacetin or a water-soluble ether of glycerol, the use of the latter for far hydrolyzed cellulose esters being described and claimed in Fordyce application Serial No. 393,664 filed May 15, 1941.

The emulsions, which were employed in the examples given herein, had a ratio of cellulose ester to silver halide of approximately six to five. This, however, may be varied somewhat in accordance with the desire of the individual operator, it only being necessary that sufficient cellulose ester is used to maintain the silver halide particles in suspension in the emulsion. In some cases it is desirable to first prepare the emulsion in a mixture of water and the lower boiling solvent and to add the higher boiling solvent shortly prior to the spraying operation. In other cases emulsions, particularly some of those having a high water content, are stable and may be kept for months at room temperature without material alteration in their properties.

The emulsion, described herein, may be applied to any surface, particularly of a fairly smooth nature, by means of any of the ordinary conventional spraying devices, such as are used for coating at the present time. It is, of course, understood that the preparation of the emulsion and the spraying is carried out in the absence of light. This invention is particularly adapted for application to metal surfaces, such as lacquered aluminum sheets to which photosensitive emulsion is applied, to assist in picturing patterns thereon. Obviously, application of the emulsion by spraying onto the surfaces of other metals, such as copper, tin, zinc, stainless steel, Monel metal or the like, or even application to non-metallic surfaces, particularly those which can be worked or machined, is contemplated by this invention. After the emulsion layer has been applied to the surface, it may be dried by a current of warm air all under light-free conditions.

The following examples illustrate the preparation of photographic emulsions adapted for spraying in accordance with this invention:

Example I

Emulsions were prepared consisting of 6 parts of cellulose acetate propionate, which had been hydrolyzed down to an acyl content of 19–26%, and 5 parts of silver bromide dissolved in a solvent mixture consisting of 50% water, 20% acetone and 30% cellosolve. One emulsion contained a ratio of cellulose ester to solvent of 1 to 30 while a second had a ratio of cellulose ester to solvent of 1 to 40. One percent of monoacetin (based on the total emulsion) was added in each case. The resulting solutions or emulsions were applied to lacquered aluminum surfaces with a spray gun. Six grams of the emulsion per square foot of surface was applied and the aluminum, containing the emulsion coating thereon, was subjected to a blast of hot air, thus drying the emulsion in about five minutes. The photosensitive coating was then exposed, processed and dried. The film on the aluminum was found to be smooth and uniform and to possess an even, glossy surface. Development and fixing were rapid and the emulsion was free of fog.

Example II

A series of emulsion solutions were prepared, the ratio of cellulose ester to solvent being 1 to 40 and of cellulose ester to silver halide 6 to 5. In each of these 30% by weight of cellosolve was present and the following percentages by weight of water and acetone were used:

	Water	Acetone
1	25	45
2	30	40
3	35	35
4	40	30
5	45	25
6	50	20

Each of these emulsions was sprayed upon a lacquered aluminum surface and it was found that a suitable film could be prepared with each of these though there was less tendency towards gloss in the dried film with the emulsions containing the higher percentages of water. The first five emulsions were not susceptible to storage at room temperature for an appreciable time; however, the emulsion No. 6 could be stored for a long time at room temperature without any deterioration occurring.

Example III

An emulsion solution was prepared, the ratio of cellulose ester to solvent being 1 to 40 and of cellulose ester to silver halide being 6 to 5. The solvent mixture consisted of the following:

	Per cent
Methyl cellosolve	35
Acetone	35
Water	30

This emulsion was applied to a lacquered aluminum surface by spraying and was dried rapidly by a blast of warm air. The film formed was uniform and smooth and the photographic properties were excellent. This solution, however, did not have the keeping qualities at room temperature of some other solutions prepared in accordance with this invention.

Example IV

An emulsion solution was prepared, as in Example 3, except that the solvent mixtures used consisted of the following:

	Per cent
Diacetone alcohol	20
Water	30
Acetone	50

Upon spraying this solution onto a metal surface, a good, fast-drying coating of smooth and glossy appearance was obtained. The processing was rapid and the emulsion was free of fog.

Example V

An emulsion solution was prepared in accordance with this invention, the ratio of cellulose ester to solvent being 1 to 25. The solvent consisted of 60% ethyl alcohol and 40% water. This solution was extremely stable, keeping at room temperature for a long period. For spraying purposes, solutions of this composition were diluted to ratios of 1 to 40, to 1 to 50. The final solvents lay within the following limits:

	Per cent
Ethyl alcohol	30–40
Water	25–50
Acetone	0–20
Cellosolve	10–30

These solutions were found to spray well and to form even smooth films on lacquered aluminum surfaces. They were processed and found to be free of fog.

Example VI

600 g. of an 11% solution of low viscosity hydrolyzed cellulose acetate propionate (14.1% acetyl, 10.7% propionyl) was prepared in a solvent composed of 50 parts by weight of water and 50 parts by weight of acetone. To this solution was added 600 cc. of water and 1500 cc. of ethyl alcohol and the temperature was adjusted to 80° F. The following solutions were prepared:

	Cubic centimeters
A. $AgNO_3$ solution containing 150 g. of $AgNO_3$	300
B. KBr solution containing 120 g. of KBr	300
C. KI solution containing 4 g. of KI	15

B and C were mixed together. Then solution A and the mixture of B and C were run into the solution of cellulose ester simultaneously in 3 minutes with stirring. 1050 g. of the 11% solution of cellulose acetate-propionate were added and the emulsion was precipitated from solution by pouring into water. It was washed thoroughly, filtered and pressed to a damp dough-like mass weighing 1200 g.

By calculation, this mass contained:

	Grams
Silver halide	175
Cellulose ester	182
Water	844

40 g. of this mass was dissolved by addition of the following solvents:

	Cc.
H_2O	90
Acetone	60
Cellosolve	45
Monoacetin	3

It was found that this emulsion could be sprayed readily to form uniform coatings of good drying properties. After exposure, development and fixation were rapid in ordinary photographic solutions.

By calculation, this solution contained approximately the following percentages by weight:

	Per cent
Water	56
Acetone	23
Cellosolve	20
Monoacetin	1+
Total	100

The ratio of cellulose ester to total solvents is, in this case, 1/36 approximately.

We claim:

1. A photosensitive emulsion adapted to be coated onto surfaces at ordinary temperature by spraying essentially consisting of a silver halide dispersed in a solution of one part of a far hydrolyzed lower fatty acid ester of cellulose in 30–50 parts of a solvent mixture consisting of 10–50% of water, 5–30% of a water-miscible organic solvent, having a boiling point above 110° C., the high boiling solvent not being present in an amount which will cause fogging of the emulsion and substantially the remainder a water-miscible organic solvent having a boiling point below 110° C. which when mixed with water is a solvent for the cellulose ester.

2. A photosensitive emulsion adapted to be coated onto surfaces at ordinary temperature by spraying essentially consisting of a silver halide dispersed in a solution of one part of a far hydrolyzed lower fatty acid ester of cellulose in 30–50 parts of a solvent mixture consisting of 10–60% of water, 5–30% of a water-miscible organic solvent, having a boiling point above 110° C., the high boiling solvent not being present in an amount which will cause fogging of the emulsion and substantially the remainder a water-miscible organic solvent having a boiling point below 110° C. which when mixed with water is a solvent for the cellulose ester together with a small proportion of a plasticizer for the cellulose ester.

3. A photosensitive emulsion adapted to be coated onto surfaces at ordinary temperature by spraying essentially consisting of a silver halide dispersed in a solution of one part of a far hydrolyzed cellulose acetate propionate in 30–50 parts of a solvent mixture consisting of 10–60% of water, 5–30% of a water-miscible organic solvent, having a boiling point above 110° C., the high boiling solvent not being present in an amount which will cause fogging of the emulsion and substantially the remainder a water-miscible organic solvent having a boiling point below 110° C. which when mixed with water is a solvent for the cellulose ester.

4. A photosensitive emulsion adapted to be coated onto surfaces at ordinary temperature by spraying essentially consisting of a silver halide dispersed in a solution of one part of a far hydrolyzed lower fatty acid ester of cellulose in 30–50 parts of a solvent mixture consisting of 10–60% of water, 5–30% of acetone and the remainder cellosolve, the three solvents being present in proportions which will not cause fogging of the emulsion.

5. A photosensitive emulsion adapted to be coated onto surfaces at ordinary temperature by spraying essentially consisting of a silver halide dispersed in a solution of one part of a far hydrolyzed lower fatty acid ester of cellulose in 30–50 parts of a solvent mixture consisting of 10–60% of water, 5–30% of acetone and substantially the remainder diacetone alcohol, the solvent mixture being of such a nature that it will not cause fogging of the emulsion.

6. A photosensitive emulsion adapted to be coated onto surfaces at ordinary temperature by spraying essentially consisting of a silver halide dispersed in a solution of one part of a far hydrolyzed lower fatty acid ester of cellulose in 30–50 parts of a solvent mixture consisting of 56% water, 23% acetone, 20% cellosolve and approximately 1% of monoacetin.

7. A method of applying a light-sensitive coating to a surface which comprises spraying onto a surface a thin coating of a solution essentially consisting of a far hydrolyzed cellulose ester dissolved in a mixture of 10–60% water, 5–30% of a water-miscible organic solvent having a boiling point above 110° C. and the remainder a water-miscible organic solvent having a boiling point below 110° C. in which solution a silver halide is dispersed all under light-free conditions.

8. A method of applying a light-sensitive coating to a surface which comprises spraying onto a surface a thin coating of a solution essentially consisting of a far hydrolyzed cellulose ester dissolved in a mixture of 56% water, 23% acetone, 20% cellosolve and approximately 1% monoacetin in which solution a silver halide is dispersed all under light-free conditions.

9. A method of applying a light-sensitive coating to a smooth metal surface which comprises spraying thereon a thin coating of a solution essentially consisting of a far hydrolyzed cellulose ester dissolved in a mixture of 10–60% water, 5–30% of a water-miscible organic solvent having a boiling point above 110° C. and the remainder a water-miscible organic solvent having a boiling point below 110° C. in which solution a silver halide is dispersed all under light-free conditions.

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