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3,218,169
METHOD OF PREPARING PHOTOGRAPHIC
EMULSIONS

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This invention relates to photography and, more par-
ticularly, to novel photosensitive products and processes
for the fabrication of same.

One object of this invention is to provide novel meth-
ods for the fabrication of silver halide photographic
emulsions.

Another object of this invention is to prepare certain
specified dispersions of silver halides useful in the prepa-
ration of photographic silver halide emulsions.

Another object of this invention is to provide a novel
means of flocking the gelatin in the preparation of photo-
graphic silver halide emulsions.

Another object of this invention is to provide a dis-
persion of silver halides from which the water-soluble
by-products may be readily removed.

Still another object of the present invention is to pro-
vide a method of washing specified silver halide dis-
persions in which substantially all of the liquid may be
removed, thus providing a substantially complete re-
moval of any water-soluble impurities therein.

Other objects of the invention will in part be obvious
and will in part appear hereinafter.

The invention accordingly comprises the several steps
and the relation and order of one or more such steps
with respect to each of the others, and the product
possessing the features, properties and the relation of
elements which are exemplified in the following detailed
disclosure, and the scope of the application of which
will be indicated in the claims.

The most common method of preparing photographic
silver halide emulsions is by reacting a water-soluble
silver salt, such as silver nitrate, with at least one water-
soluble halide, such as potassium or sodium bromide,
preferably together with potassium or sodium iodide, in
an aqueous solution of a gelatin colloid peptizing agent.
The dispersion of silver halide thus formed contains
water-soluble salts as a by-product of the double de-
composition reaction, in addition to an unreacted excess
of either of the initial salts. It has been considered
desirable in the case of photographic emulsions that the
water-soluble salts present in the emulsion be reduced
in concentration. It has generally been the practice,
where gelatin has been used as a protective colloid, to
remove the soluble material therefrom by setting the
gelatin dispersion by means of chilling, noodling the so-
set dispersion, and washing the noodles with cold water
or where a gelatin derivative has been employed co-
agulating the gelatin derivative, separating the coagulant
from the supernatant liquor, and washing the separated
coagulant with water at such temperature as to keep
the coagulant from melting.

The present invention is concerned with the prepara-
tion of photographic emulsions having silver halide
as the sensitive material and wherein the silver halide is
prepared and dispersed in an aqueous solution of gela-
tin. Subsequent to ripening of the emulsion for the
desired length of time, a soluble polymer, which pos-
sesses the property of being insolubilized upon complex-
ing with a hydrogen bonding complexant, is added to
the dispersion. After distributing the polymer through-
out the dispersion to ensure sufficient chain entangle-

ment with the gelatin, the hydrogen bonding compound
is added as a complexing agent. Such complexing agents
render the polymer insoluble in situ whereby the polymer
complex precipitates causing the gelatin to floc, probably
as a co-precipitate due to a physical chain entanglement
of the polymer and the gelatin. The gelatin and polymer-
complexant are then removed from the supernatant liquor
and washed with cold water and/or dilute, cold caustic
solution to remove the water-soluble by-products and
other impurities including the polymer and the polymer-
complexant. The silver halide-gelatin agglomerates may
then be formulated into a photographic emulsion by re-
dispersion in a gelatin or the like matrix or vehicle.

The term "gelatin" as utilized herein is intended to
signify the art-accepted designation of the photographic
colloid binder derived from collagen and comprising a
proteinaceous substance. The term is intended to include
both acid and alkali process gelatins.

The term "gelatin" is also intended to include any
other product substantially identical therewith, as for
example, where such product is produced synthetically.

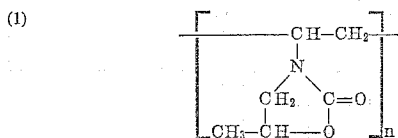
In carrying out the present invention, the silver halide
is prepared in an aqueous solution of gelatin as the
peptizer. The silver halide is preferably prepared by
reacting a water-soluble silver salt, preferably silver ni-
trate, with at least one water-soluble halide salt, pref-
erably sodium or potassium bromide, most preferably
in combination with sodium or potassium iodides, in an
aqueous solution of a gelatin colloid peptizing agent.
Subsequent to ripening for the desired length of time, a
water-soluble polymer capable of being precipitated with
hydrogen bonding complexing agents, preferably a poly-
vinyl heterocyclic polymer, e.g., oxazine, oxazoline,
oxazolidinone or pyrrolidone polymer, is dispersed in the
solution. A suitable complexant, i.e., a hydrogen bond-
ing agent that will precipitate the polymer, e.g., an aro-
matic acid or aromatic hydroxyl compound, is added,
thereby rendering the polymer insoluble and causing
the gelatin-silver halide dispersion to floc, entrapped by
the precipitating polymer. The flocked material can
then be readily separated and washed with water. The
water-soluble salts and by-products are thereby readily
removed along with the complexed and uncomplexed
polymer. Preparation of the emulsion can then be con-
tinued in the conventional manner.

The silver halide crystals may be prepared in the
gelatin peptizing agent in any of the normal methods
for the preparation of silver halide dispersions, as for
example by introducing a stream of an aqueous solution
of silver nitrate and a stream of an aqueous solution
of at least one alkali-metal halide, preferably potassium
or sodium bromide, and potassium or sodium iodide,
into a constantly agitated solution of the peptizing agent.
Alternatively, the gelatin solution may be combined
with one of the reactants and the other reactants may
be introduced with stirring. After the silver halide has
formed, any ripening desirable may be effected. Subse-
quent to ripening, the solution is cooled, preferably to a
temperature of 30 to 35° C. The polymer is then dis-
solved and thoroughly dispersed in the solution. Upon
addition of the complexant, the precipitating polymer
carries down the silver halide-gelatin dispersion. The
coagulum, substantially a physical combination of silver
halide-gelatin and complexed polymer, uncomplexed
polymer and various salts, may then be readily sepa-
rated from the liquid by any one of several techniques.

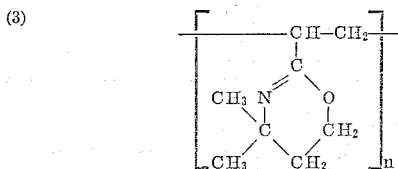
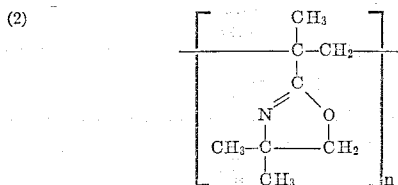
In simplest form, the supernatant liquid may be re-
moved by decantation. The coagulum may then be
washed by cold water. After washing, the coagulum
consists of silver halide and gelatin, any other water-
soluble materials which may be present, and a small

amount of residual salts dissolved in any water trapped in the coagulum. In addition, a small amount of polymer or polymer complex may be physically trapped by the flocked gelatin. However, it has been found that the photographic utility of the silver halide-gelatin coagulum has not been deleteriously affected by such a residue. For example, in testing emulsions made by the method of this invention, fog levels were low, no desensitization was apparent, and, when treated with gold sensitizer, good speed response was found.

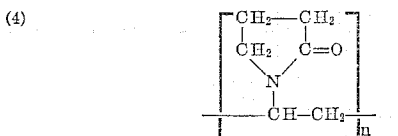
The preferred polymer employed in the preparation of the emulsion of this invention is a cold water-soluble, alkali-soluble, polyvinyl heterocyclic polymer capable of being precipitated by a complexant that is a hydrogen bonding agent. In a preferred embodiment, such polymers contain a 5-methyl-2-oxazolidinone ring, e.g., poly-N-vinyl-5-methyl-2-oxazolidinone. Polymers of this type are commercially available from the Dow Chemical Company, Midland, Michigan, under the trade name "Devlex Resins." As an example of such a polymer mention may be made of a polymer of the formula:



As examples of other suitable polyvinyl heterocyclic polymers useful in this invention mention may be made of oxazine, oxazoline and pyrrolidone polymers, for example, polymers of the formulae:



and



The polymers of Formulae 2 and 3 are disclosed in U.S. Patent No. 2,897,182, issued July 28, 1959. Polymers of Formula 4 are commercially available from General Aniline and Film Corp., Binghamton, New York.

The polymers of the aforementioned type readily complex with hydrogen bonding agents and precipitate quantitatively. Thus, floccing can be carried out easily and quickly using the process of this invention. As examples of hydrogen bonding agents used as complexants, mention may be made of aromatic hydroxyl compounds such as phenols, resorcinols, phloroglucinols, amines, aromatic acids such as benzoic acid and sulfonic acids, mercaptobenzothiazoles, thiocarbanilides, etc. The concentration of complexant necessary to flocculate is determined on the basis of the particular complexing agent used, but should be at least approximately 2% of the total emulsion on a weight/volume basis, i.e., 2 grams/100 cc. of total emulsion.

Since the polymers suitable for use in this invention are very soluble in cold water and generally become increasingly insoluble in water above 40° C., the temperature

of the silver halide-gelatin dispersion should preferably be maintained below this point to ensure complete solubility and adequate distribution of the polymer on its addition to the dispersion. After the addition of the complexant to the dispersion, agitation is continued to provide the necessary interaction between the polymer and complexant. The agitation is then stopped and the floc allowed to settle. In order to prevent the formation of a gummy mass of gelatin particles, before the agitation is stopped and the floc allowed to settle, the temperature of the dispersion should be below the melting point of the gelatin.

In the preparation of some emulsions it may be desirable to add the complexant and polymer at temperatures high enough to provide for thermal agitation of the dispersion with the resulting chain entanglement of the polymer and gelatin and still floc at temperatures below the melting point of the gelatin. This may be accomplished by adding the complexant in salt form, e.g., sodium phenate, sodium benzoate or potassium acid phthalate, which does not form an insoluble complex with the polymer, cooling the solution to the desired temperature, and then carrying out the flocculation by regenerating the complexant by acidification whereby it will readily complex with the polymer. For example, sodium phenate or potassium acid phthalate will not insolubilize the polymer, but when converted to phenol or phthalic acid by acidification by sulfuric acid, for example, the regenerated complexant will precipitate the polymer.

The polymer is preferably added to the silver halide-gelatin dispersion as a 10% solution in a ratio of 5 to 35 parts of polymer to 10 parts of gelatin. In a preferred embodiment, the ratio is 6 parts of polymer to 10 parts of gelatin, on an air dry weight basis. After addition of the polymer, agitation of the dispersion is carried on for 2 to 5 minutes. The complexant is then added with continuing agitation and cooling. The coagulum then settles and is ready to be separated and washed.

As described above the precipitated coagulum may be washed with cold water to remove by-products, excess soluble salts, as well as the polymer and polymer complex. Since the polymer complex is water-insoluble, its removal is accomplished by a stream of cold water which displaces the polymer-polymer complex equilibrium. It may be desirable, therefore, in order to accelerate the washing process, to precede the cold water wash with an initial caustic wash to remove the water-insoluble polymer complex.

As used herein, the term "polymer complex" is intended to signify the reaction product of the polymer and the hydrogen bonding agent complexant.

It can be readily seen that this invention provides a novel process for the preparation of photosensitive emulsions that does not involve the use of gelatin derivatives and their attendant disadvantages or any treatment of the gelatin that might interfere with the photographic employment of the emulsion. A minimum of steps is necessary in an easy and rapid process that utilizes materials that can be substantially removed from the silver halide-gelatin emulsion by a simple wash. In addition, any small amount of materials remaining entrapped in the emulsion after washing does not interfere with the photographic employment of the emulsion.

It is apparent that one advantage of the "flocculation" technique for the preparation of photographic emulsions described herein is that the concentration of silver halide in the final emulsion may be adjusted to any desired value without reference to the quantity of water, silver halide and gelatin employed in the initial reaction for the preparation of the silver halide dispersion. Thus, concentrated emulsions may be readily prepared. Dried emulsions may be prepared for storage and shipment without any necessity of extensive evaporation of water or reduction of the water content of the dispersed silver halide and without the necessity of using concentrated salt solu-

tions or organic solvents. The coagulum prepared is especially suitable for the preparation of dried emulsions, since it may be obtained in a state nearly free of excess water, and therefore the drying operation is simplified and rendered less expensive. The coagulum, either prior to or subsequent to restoration of its gel properties, thus may be obtained in a suitable form for this purpose, and the dried coagulum may be readily redispersed at any time.

The following non-limiting examples illustrate the preparation of the emulsions within this invention.

Example A

To a solution of 230 ml. of water, 34 g. of potassium bromide, 2 g. of potassium iodide and 7 g. of gelatin, maintained at a temperature of 64° C., were added over a one-minute period, 234 ml. of a solution comprising 410 ml. of water and 42 g. of silver nitrate. Another 184 ml. of the silver nitrate solution were added over a 25-minute period. The emulsion was then cooled to 50° C. and ripened for 30 minutes. Ripening was then reduced by cooling the solution to between 30 and 35° C.

Example I

To the emulsion in Example A, there was added, at a temperature of 35° C., 42 ml. of a 10% solution of poly-N-vinyl-5-methyl-2-oxazolidinone (commercially available from the Dow Chemical Company, Midland, Michigan, under the trade name Devlex 130) and the mixture was stirred for 3 minutes. 180 ml. of 10% potassium acid phthalate solution were then added and stirring continued for 3 minutes. With continued stirring the solution was then cooled below 20° C. The pH was then adjusted to 2.8 with 2 N sulfuric acid. The resulting coagulum was then separated and washed with 1500 ml. of cold water (15° C. or lower) to which had been added 100 ml. of 1 N sodium hydroxide. A cold water wash was then carried out.

Example II

To 100 ml. of the emulsion prepared as in Example A, there was added, at a temperature of 35° C., 6.5 ml. of a 10% solution of 4,4-dimethyl-2-isopropenyl-oxazoline and the mixture was stirred for 5 minutes. After cooling the emulsion to between 15 and 20° C., 25 ml. of a 10% resorcinol solution were added with stirring. The precipitate was allowed to settle, separated and washed as in Example I.

The resultant emulsions were sensitized, the desired additives incorporated therein, and the emulsions coated and processed according to conventional procedures known in the emulsion manufacturing art.

The emulsions of this invention may be coated onto various types of rigid or flexible supports, for example, glass, paper, metal, polymeric films of both the synthetic types and those derived from naturally occurring products, etc. Especially suitable materials include paper; aluminum; polymethacrylic acid methyl and ethyl esters; vinyl chloride polymers; polyvinyl acetals; polyamides such as nylon; polyesters such as the polymeric films derived from ethylene glycolterephthalic acid; and cellulose derivatives such as cellulose acetate, triacetate, nitrate, propionate, butyrate, acetate-propionate, or acetate-butyrate.

The light-sensitive material of the photographic emulsions comprises a compound of silver, for example, one or more of the silver halides of which silver chloride, silver bromide and silver iodide are examples. The preferred silver halide emulsion comprises a silver iodobromide emulsion. It will be understood that preferred silver halide emulsions of varying halide concentration may be advantageously employed.

The emulsions of the present invention may be chemically sensitized by any of the accepted procedures. For example, the emulsions may be digested with naturally

active gelatin, or sulfur compounds can be added such as those described in U.S. Patents Nos. 1,574,944, 1,623,499 and 2,410,689.

The emulsions may also be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium, and platinum, all of which belong to Group VIII of the Periodic Table of Elements and have an atomic weight greater than 100. The salts may be used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in U.S. Patent No. 2,448,060, and as antifoggants in higher amounts, as described in U.S. Patents Nos. 2,566,245 and 2,566,263.

The emulsions may also be chemically sensitized with gold salts as described in U.S. Patent No. 2,399,083 or stabilized with gold salts as described in U.S. Patents Nos. 2,597,856 and 2,597,915.

The emulsions may also be chemically sensitized with reducing agents such as stannous chloride as described in U.S. Patent No. 2,487,850; amines such as diethylenetriamine as described in U.S. Patent No. 2,518,698; polyamides such as spermine as described in U.S. Patent No. 2,521,925; or bis-(β -aminoethyl)-sulfide and its water-soluble salts as described in U.S. Patent No. 2,521,926.

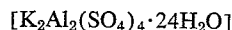
The emulsions may also be stabilized with the mercury compounds of U.S. Patents Nos. 2,728,663, 2,728,664 and 2,728,665.

The emulsions may also be optically sensitized with cyanine and merocyanine dyes as described in U.S. Patents Nos. 1,846,301, 1,846,302, 1,942,854, 1,990,507, 2,112,140, 2,165,338, 2,493,747, 2,493,748, 2,503,776, 2,519,001, 2,666,761, 2,734,900, 2,739,149 and 2,739,964.

The emulsions may also contain speed-increasing compounds of the quaternary ammonium type as described in U.S. Patents Nos. 2,271,623, 2,288,226 and 2,334,864; and of the polyethylene glycol type as described in U.S. Patent No. 2,708,162.

Where desired, suitable antifoggants, restrainers, accelerators, preservatives, coating aids, and/or stabilizers may be included in the composition of the emulsions.

Hardening agents such as inorganic agents providing polyvalent metallic atoms, especially polyvalent aluminum or chromium ions, for example, potash alum



and chrome alum $[\text{K}_2\text{Cr}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}]$ and organic agents of the aldehyde type such as formaldehyde, glyoxal, mucochloric acid, etc., the ketone type such as diacetal, and the quinone type, may be incorporated in the emulsions according to procedures well known in the art.

The term "photosensitive" and other terms of similar import are herein employed in the generic sense to describe materials possessing physical and chemical properties which enable them to form usable images when exposed to actinic radiation.

It has been stated above that any residue of polymer that may remain in the silver halide gelatin particles after washing due to physical entrapment does not deleteriously interfere with the photographic employment of the emulsion. In fact, speed-increasing and fog-depressing characteristics were imparted to test emulsions, by the presence of such polymer.

Since certain changes may be made in the above process and product without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A method of preparing silver halide dispersions which comprises the steps of mixing together a water-soluble silver salt and at least one soluble halide in an aqueous solution of a gelatin peptizing colloid, thereby forming a silver halide-gelatin dispersion, adding a water-soluble polymer selected from the group consisting of polyvinyl oxazines, polyvinyl ozazolines, polyvinyl

oxazolidinones and polyvinyl pyrrolidones to said silver halide dispersion in gelatin and coagulating the mixture by adding a hydrogen bonding agent selected from the group consisting of phenols, resorcinols, aromatic acids, amines, mercaptothiazoles, phloroglucinols and thio-
 5 carbanilides, whereby a water-insoluble reaction product of said water-soluble polymer and said hydrogen bonding agent is formed, separating the resulting precipitate from the liquid portion of the mass, and washing the separated precipitate with a cold water wash, thereby rendering it
 10 substantially free of said reaction product of said polymer and said hydrogen bonding agent.

2. A method as described in claim 1 wherein said water-soluble silver salt comprises silver nitrate.

3. A method as defined in claim 1 wherein said water-soluble halide is selected from the group consisting of
 15 sodium bromide, sodium iodide and potassium iodide.

4. A method as defined in claim 1 wherein the polymer-to-gelatin ratio is within the range of about 5 to 35 parts
 20 of polymer to 10 parts of gelatin.

5. A method as defined in claim 1 wherein said cold water wash is immediately preceded by a caustic wash.

6. A method as defined in claim 1 wherein said hydrogen bonding agent is added to said mixture as a salt thereof and free hydrogen bonding agent is provided by
 25 acidifying said mixture.

7. A method as defined in claim 1 including the step of mixing said separated precipitate with a polymeric protective colloid for said silver halide gelatin.

8. A method as defined in claim 7 including the step of
 30 coating said mixture on a support.

9. A method as defined in claim 7 wherein said polymeric protective colloid comprises gelatin.

10. A method of preparing a silver halide dispersion which comprises the steps of mixing together a water-soluble silver salt and at least one soluble halide in an
 35 aqueous solution of a gelatin peptizing colloid, thereby forming a silver halide-gelatin dispersion, adding an aqueous

solution of poly-N-vinyl-5-methyl-2-oxazolidinone and potassium acid phthalate to said silver halide dispersion in gelatin, coagulating the dispersion by acidifying and separating the resulting precipitate from the liquid portion of the mass, and washing said precipitate with an initial caustic wash, followed by a cold water wash, thereby removing substantially all of the reaction product of said poly-N-vinyl-5-methyl-2-oxazolidinone and said potassium acid phthalate.

11. A method of preparing a silver halide dispersion which comprises the steps of mixing together a water-soluble silver salt and at least one soluble halide in an aqueous solution of a gelatin peptizing colloid, thereby forming silver halide-gelatin dispersion, adding an aqueous solution of poly-4,4-dimethyl-2-isopropenyl-oxazoline to the silver halide dispersion in gelatin, coagulating by adding resorcinol to said dispersion, separating the resulting precipitate from the liquid portion of the mass, and washing said precipitate with an initial caustic wash, followed by a cold water wash, thereby removing substantially all of the reaction product of said poly-4,4'-dimethyl-2-isopropenyl-oxazoline and said resorcinol.

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