

UNITED STATES PATENT OFFICE.

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TINTING PROCESS AND PRODUCT THEREOF.

1,279,276.

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No Drawing.

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To all whom it may concern:

Be it known that I, JOHN I. CRABTREE, a resident of Rochester, in the county of Monroe, State of New York, have invented certain new and useful Improvements in Tinting Processes and Products Thereof, of which the following is a specification.

This invention relates to a process of coloring or tinting light transmitting or transparent bodies by means of colored inorganic salts in finely divided or colloidal condition. It also relates to the product of this process. More particularly it relates to the coloring or tinting of "colloids" such as gelatin, cellulose and its derivatives, albumen, soluble starch, dextrin, water soluble gums, etc. For example, my process may be used for tinting the gelatin layer of motion picture positive films or lantern slides, or for related light-modifying uses.

The objects of my invention are to provide a cheap process of tinting by inorganic means in which the color and depth of the tint will be under very exact control; in which a satisfactory tint may be easily and precisely duplicated; in which the wearing qualities of the product will not be impaired; in which the colors will be stable to light, and in which the colors in certain instances may be removed chemically if desirable. Other objects are to provide a product in which an inorganic tint is of the color and depth desired, which has unimpaired wearing qualities, in which the colors are stable to light and in which the colors may in certain instances be removed by chemical means or solvents. Further objects will hereinafter appear.

Inasmuch as present conditions in the dye-stuff industry render it difficult to obtain the necessary organic dyes for staining motion picture positive films to give special color effects, a cheaper way of obtaining the desired result has been sought after in the motion picture industry. My process is well adapted to staining such film. Therefore, I have chosen as examples of my invention, three typical applications of it to the motion picture art. It should be understood, however, that it is not limited thereto except as indicated in the claims.

Motion picture positive film ordinarily comprises a flexible transparent base on which is a layer of transparent gelatin, and in the gelatin are the small particles of sil-

ver constituting the image, this silver image being substantially opaque in its gradations. Color effects in such film have been obtained chiefly by two methods: First, toning the silver image by changing the color of the particles thereof without appreciably or intentionally changing the color of the gelatin; second, tinting the gelatin itself. This second method has been performed hitherto by using expensive organic dye-stuffs as the agents for staining the gelatin. The examples of my method, which will be given, relate chiefly to a modification of this second method in which inorganic coloring matter is substituted for the more expensive organic dyes. It is to be understood that even if a certain extent of toning or alteration in the color of the silver image should incidentally take place in my method, it is usually undetectable in the preferred form of my invention, and in any event is not material.

Broadly stated I precipitate colored metallic salts within the colloidal layer. To this end I use two solutions, one containing a soluble salt of the metal which is to enter into the precipitate and another containing a soluble salt which furnishes the acid radical which is to enter into the precipitate. The metals which furnish the best compounds appear to be iron, uranium, lead, copper, bismuth, cadmium, tin, tungsten, molybdenum, silver, mercury, cobalt, or nickel. The best acid radicals appear to be those which form ferrocyanids or sulfids depending, of course, on the metal ion employed.

First example—blue tint.

Using any usual or preferred apparatus for fluid treating motion picture film, the film strip to be tinted is immersed for five minutes in a 1% solution of ferric-alum, then rinsed and then immersed in a 1% solution of potassium ferrocyanid until the desired tint is obtained. The film is then well washed for 10 to 15 minutes. The control of the tint is obtained by regulating several factors. A blue tint due to colloidal ferric ferrocyanid is obtained.

The depth of the tint obtained increases with increasing concentration of the ferric-alum, and the strength of the solution which may be employed, of course, can be varied to suit the operator's needs. I have found,

however, that a 1% solution is sufficiently strong in practice and is usually preferable to stronger solutions which tend to give a too deep tint for ordinary projection.

5 The depth of the tint increases with the time of immersion within certain limits. With solutions of the strength given, prolonged immersion after 3 to 5 minutes has very little effect.

10 The time of rinsing is an important factor. Using the solutions given, one or two minutes washing is necessary for weak tints, while for stronger tints a mere quick rinsing is all that should be given. While the practice is not usually to be recommended, the rinsing may sometimes be dispensed with.

The nature of the final tint is independent of the concentration of the potassium ferrocyanid solution provided the film be immersed for a sufficient length of time, the maximum effect with a 1% solution being usually produced within five minutes. A shorter immersion will, of course, give 25 lighter tints, although this way of modifying the tint is not as desirable as the varying of the time of rinsing. It tends to cause intensification of tinting during subsequent washing.

30 The temperature of the baths has a considerable effect, a shorter time of immersion being necessary in the ferric-alum at high temperature. Too high temperatures, however, tend to produce reticulation or puckering of the gelatin, and a temperature of 35 about 70° F. is more satisfactory.

Second example—orange tint.

The film is immersed in a 1% solution of 40 uranium nitrate, rinsed and then immersed in a 1% solution of potassium ferrocyanid in the same manner as outlined above in the first example. The factors which affect the tinting are similar to those described in connection with the blue tinting and need not 45 be repeated. An orange tint due to colloidal uranium ferrocyanid is obtained.

It may be noted that the first and second tinting methods may be to a certain extent 50 combined to produce darker tints, a small amount of ferric-alum being added to the uranium nitrate bath.

Third example—sulfid tint.

55 The film is immersed for a suitable time, say two minutes, in a 1% solution of lead nitrate, rinsed, and then immersed in a 5% solution of sodium sulfid for a suitable time, which may be about two minutes. To avoid 60 softening of the film with these particular solutions, the temperature should not exceed 70° F. A tint due to colloidal lead sulfid is obtained.

Other nitrates, such, for instance, as 65 cupric nitrate and bismuth nitrate may be

substituted for the lead nitrate in this method. The factors of control in this method are the same as those of the previous examples.

It is important that the baths should not 70 quickly deteriorate, and I have experimentally found that the baths recommended possess long life and are insensitive to light.

Folding tests have indicated that the wearing qualities of the film are not affected by 75 this method of tinting. Exposure to light by the usual tests has also shown that the tints do not materially alter within periods of time corresponding to the commercial life of the film. 80

The iron and uranium ferrocyanids, which are formed in the first and second examples given above, are soluble in alkali, such as alkali carbonate, caustic alkali, etc. This is a valuable feature as it enables the operator 85 to remove the tint wholly or partially should he find the color unadapted to the particular subject portrayed by the film. Furthermore, he may tint the film for one exhibit and decolorize it for another exhibit where different lighting conditions prevail. Since the 90 silver image is not materially altered by the above solution it will not be dissolved or altered when the tinting salts are dissolved out. It will be noted from these examples that 95 I carry out my tinting process independently of any light action, making slow printing operations unnecessary.

The tint is quite uniformly distributed throughout the gelatin. Consequently my 100 method may be used not only to tint an even layer of gelatin but may be used to tint gelatin layers of varying thickness such as are produced by printing bichromated gelatin under a negative and dis- 105 solving away the soluble gelatin in the well known way to form a gelatin relief image. A monochrom image of desired tint can thus be obtained.

The theory of the method seems to be that 110 colloidal substances, such as gelatin, have an enormous number of minute or capillary passages therein into which diffuses the first solution, which contains the ions of that metal which is to enter into the precipitated 115 colored particles constituting the tint. Rinsing removes such solution from the surface of the gelatin and, if prolonged diminishes the concentration of the metallic ions in some or all of the passages of the gelatin. When 120 the gelatin is next placed in the second or precipitating solution containing the anions which are to enter into the precipitate, said solution diffuses through the passages in the gelatin and the anions combine with the 125 metallic ions. The result is a precipitate of colored particles wherever the two ions meet and, due to the minute passages in which they are formed and to the so called protective action of the colloidal gelatin, these par- 130

5 ticles cannot agglomerate but remain dis-
persed in a finely divided or colloidal state.
The individual particles cannot be seen by
the naked eye or under a low power magni-
ficer, the tint appearing homogeneous. Wash-
ing removes the soluble salts which remain
after the precipitate is formed and it may
also check overtinting. While this is the
theory of the action as now understood, a
10 knowledge of the true theory is, of course,
not indispensable in practising my inven-
tion.

It will be seen from the examples herein-
above given that my tinting process is par-
15 ticularly applicable to colloidal layers hav-
ing a definite image already formed therein.
The colloid is still transparent or light trans-
mitting after tinting, but the light which
can pass through it will, of course, be col-
20 ored. This is particularly important in pro-
jection work. Thus with the ferric ferro-
cyanid blue tint, bluish light will be trans-
mitted, and if the incident light is white,
certain wave lengths or components thereof
25 will be absorbed or modified by the colored
particles in the tint, so that only the wave
lengths or components corresponding to the
blue color will pass through.

I claim:

30 1. The process of tinting independently
of light action a gelatin layer containing
a silver image, which consists in precipi-
tating sufficient colored inorganic salts in
dispersed and finely divided condition in
35 said gelatin independently of said image to
permit a substantially full transmission of
light waves producing the desired tint but
substantially preventing the transmission
of other light waves.

40 2. A process of treating independently
of light action a transparent colloid con-
taining an opaque image, which consists of
diffusing therein a soluble salt of a metal ca-
pable of entering into a colored inorganic
45 precipitate and diffusing through said col-
loid a solution of a compound capable of
furnishing a component of said colored pre-
cipitate, the salt and compound reacting
in the colloid independently of said image
50 to produce dispersed and finely divided col-
ored inorganic insoluble particles produc-
ing a substantially transparent tint.

3. The process of tinting independently
of light action a gelatin layer containing an
55 opaque image which consists in treating the
same in a solution of a soluble salt of a
metal capable of entering into a colored in-
soluble compound, rinsing said gelatin and
treating said gelatin in a bath of a soluble
60 inorganic reagent which reacts to form a
colored insoluble compound of said metal,
whereby a colored inorganic salt is pro-
duced in the gelatin independently of said
image in finely divided and dispersed con-
dition.

4. The process of tinting a body of a
transparent colloid which consists in dif-
fusing in said body a solution of ferric-
alum and subsequently diffusing therein a
solution of potassium ferrocyanid to pro-
70 duce a chemical reaction within the body
and form dispersed and finely divided parti-
cles of ferric ferrocyanid giving a blue
substantially transparent tint by transmit-
ted light.

5. The process of treating gelatin contain-
ing a photographic image, which consists in
treating the same in a ferric-alum solution,
rinsing the same, treating the same in a solu-
tion of potassium ferrocyanid until a tint
80 is obtained, and washing the same to elimi-
nate the remaining soluble compounds,
whereby a substantially transparent tint is
produced.

6. The process of treating photographic
85 gelatin, which consists in treating the same
in a solution of ferric-alum, rinsing the
same, treating the same in a solution of
potassium ferrocyanid until colloidal parti-
cles forming a tint are produced, washing
90 the same, and finally controlling the color
effect by treating the tinted gelatin in a
bath containing a solvent of the particles of
the tint.

7. The process of tinting gelatin contain-
95 ing an image, which consists in treating the
same in a diluted solution of ferric-alum,
rinsing the same, treating the same in a di-
luted solution of potassium ferrocyanid un-
til a tint is obtained, washing the same,
100 and finally controlling the tint by treating
the tinted gelatin in an alkali carbonate so-
lution.

8. The process of coloring gelatin associ-
ated with the image of a photograph, which
105 comprises diffusing iron ions through said
gelatin by treating the gelatin in a bath of
ferric-alum, rinsing the surface of said
gelatin to remove the excess of ferric-alum
solution, diffusing ferricyanid ions through
110 the gelatin in a bath of potassium ferro-
cyanid to produce a colloidal blue precipi-
tate of ferric ferrocyanid dispersed through
said gelatin, and washing the gelatin to re-
move the soluble salts remaining after the
production of the colloidal precipitate, said
treatments being composed and controlled
to leave the image of the photograph sub-
stantially unaltered.

9. The process of coloring gelatin associ-
120 ated with the image of a photograph,
which comprises treating said gelatin in a
bath containing a soluble salt of a metal
capable of entering into a colored colloidal
precipitate, thereby diffusing the ions of
125 the metal through said gelatin, rinsing the
excess of said solution from the surface of
the gelatin, treating said gelatin in a bath,
containing negative ions capable of uniting
with said metallic ions to form colored in-

soluble inorganic compounds, until said negative ions diffuse through said gelatin and combine with the diffused metallic ions to form a colloidal colored precipitate appearing as a homogeneous tint to the naked eye, and finally washing out the soluble salts remaining after the formation of the colloidal precipitate, the said treating baths being composed and controlled to leave the photographic image substantially unaltered.

10. As an article of manufacture, a film comprising a transparent base, a transparent gelatin layer thereon containing a silver image, and inorganic colored salts in finely divided condition dispersed evenly in said gelatin to produce a substantially transparent tint.

11. As an article of manufacture, a light transmitting colloid having an image therein, and also having therein finely divided and dispersed inorganic colored salts to produce a tint.

12. As an article of manufacture, a motion picture positive film comprising a transparent flexible base, a layer of transparent gelatin thereon containing a photographic opaque image and colored inorganic salts as a substantially transparent tint in colloidal condition distributed in said gelatin.

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Witnesses:

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