

Jan. 2, 1945.

L. V. CHILTON ET AL

2,366,439

PHOTOGRAPHIC MATERIALS

Filed April 21, 1941

Fig. 1

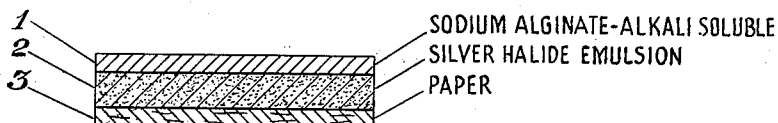


Fig. 2

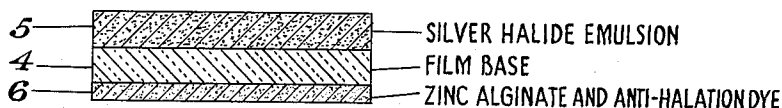


Fig. 3

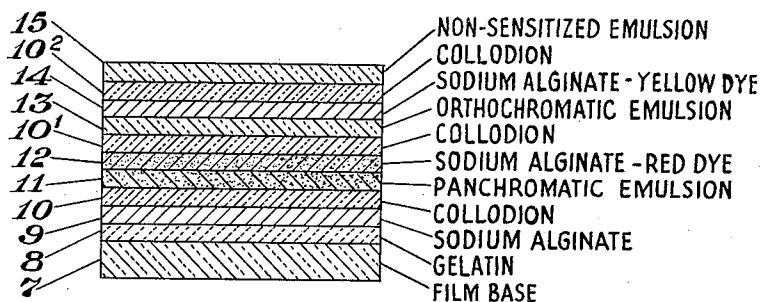


Fig. 4

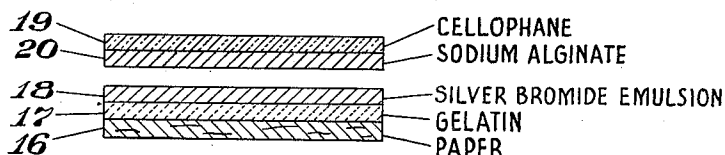


Fig. 5

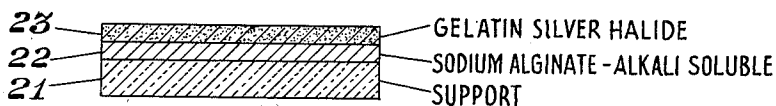
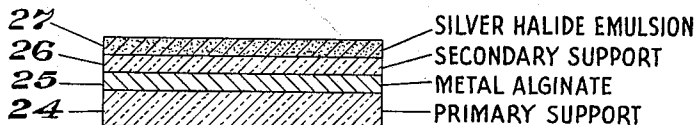


Fig. 6



Leonard Vincent Chilton

Duncan Pax Woosley

INVENTORS

BY
Lynn B. Morris
ATTORNEY

UNITED STATES PATENT OFFICE

2,366,439

PHOTOGRAPHIC MATERIALS

Leonard Vincent Chilton and Duncan Pax Woosley, Ilford, England, assignors to Ilford Limited, Ilford, England, a British company

Application April 21, 1941, Serial No. 389,690
In Great Britain May 6, 1940

9 Claims. (Cl. 95—8)

This invention relates to materials comprising colloid layers and particularly to photographic materials comprising colloid layers.

According to the present invention photographic materials comprise layers of metal alginates which are insoluble in water but soluble in ammonia solution or dilute sodium carbonate solution. It has been discovered that such water-insoluble layers form excellent, readily removable, supercoats for photographic emulsions and serve in that capacity to prevent or reduce the formation of stress marks on the emulsion. Suitably dyed, such layers also serve as satisfactory filter layers and antihalation layers. The water-insoluble alginates of this invention also serve as media for the dispersion of materials other than dyes, e. g. as media for an X-ray fluorescent material supercoated on a gelatino silver halide emulsion on a film, plate or paper to be used for radiography. Moreover, the alginate layers serve as excellent stripping layers.

Examples of insoluble metal alginates which may be employed according to this invention are the alginates of cobalt, nickel, copper, chromium, zinc, vanadium, tungsten, silver, aluminium, molybdenum and cadmium. All of these are readily soluble in ammonia solution and aluminium, chromium and vanadium alginates in particular are readily soluble in dilute sodium carbonate solutions.

Another alginate which may be employed is calcium alginate and layers of this may conveniently be formed in situ where they are to be formed as coatings on gelatin layers. Thus, it has been discovered that if over a layer of normal gelatin there is coated a layer of a water-soluble salt of alginic acid, the alginate layer sets to a hard, water-insoluble form. Normal gelatin contains calcium salts and the setting of the alginate layer is apparently due to the migration of calcium ions from the gelatin into the alginate layer with the resulting formation of a calcium alginate gel. Calcium alginate is readily soluble in dilute sodium carbonate.

The metal alginate layers of this invention may be formed by coating the surface which is to carry such a layer with a solution of a metal alginate in dilute sodium carbonate solution or in ammonia solution. Preferably, however, the metal alginate layer is formed by coating or impregnating the surface which is to carry the metal alginate layer with a solution of a soluble salt of the metal of which the alginate is desired, then treating the surface with an aqueous solution of a water-soluble alginate and then wash-

ing and drying the product. Alternatively, these two coating operations may be carried out in the reverse order. As indicated above, where it is desired to form a calcium alginate layer as a coating on a normal gelatin layer a separate treatment with a calcium salt is unnecessary, and it is sufficient to coat the gelatin layer (either wet or dry) with a solution of a water-soluble alginate.

Any water-soluble salt of alginic acid may be used for the production of water-insoluble metal alginates in accordance with this invention. Suitable examples are the sodium, potassium and other alkali metal salts, ammonium salts, magnesium salts and salts with organic bases, e. g. triethanolamine salts. One of the most convenient salts for such use is commercial sodium alginate, for example the product sold under the trade-mark "Manucol," which gives very satisfactory results. Alginic acid salts may be obtained with various physical characteristics depending upon the degree of de-polymerisation of the alginic acid. Thus, sodium alginate may have a viscosity varying from 20-400 centipoises (estimated on a 1% solution in distilled water at 15° C.). The most suitable strength of the solution employed for coating purposes in accordance with this invention will therefore vary with the viscosity characteristics of the alginic acid salt employed; neither a very low viscosity nor a very high viscosity solution is desirable since either may lead to coating difficulties.

In order to facilitate the coating of the alginate solution, it is preferable to include in the solution a proportion of a wetting agent. Suitable agents are, for example, saponin, potassium oleate, Turkey red oil, sodium lauryl sulphate and the commercial wetting agents sold under the trade names Igepon T, Santomerse D, Aresklene 375 and Perminol W. In general, using sodium alginate having a viscosity of 20-40 centipoises (estimated on a 1% solution in distilled water at 15° C.) as a 0.6% aqueous solution for coating, the minimum concentration of the wetting agent desirable is from 0.01% to 0.05% though higher concentrations e. g. up to 2% may frequently be employed with advantage. It will be appreciated that the optimum concentration of wetting agent will depend inter alia on the nature of the wetting agent itself.

The metal alginate layers of this invention may be employed as supercoats over gelatino-silver halide emulsions carried on paper, glass or film supports and serve in this relationship to prevent or reduce the formation of stress

marks on the emulsion. Moreover, since the metal alginate layers of this invention are soluble in ammonia solution or in dilute sodium carbonate solutions, they may be removed in the development of the gelatino-silver halide emulsions in alkaline developers or by a subsequent treatment with an ammonia solution. Thus, for example, the emulsion surface of a photographic printing paper may be supercoated with a layer of a metal alginate according to this invention, the supercoat serving to reduce the risk of stress marks being formed, and this layer may be removed during development or by subsequent treatment with ammonia solution yielding prints which have no supercoat and which are therefore of especial value in the Carbro process, where intimate contact of the silver image layer with a sensitised pigment layer must be obtained, in the bromoil process, in the processes for obtaining photographic relief images described in application No. 379,357, filed February 17, 1941, entitled "The production of gelatin layers."

The metal alginates of this invention have good adhesive properties and may form intermediate layers in multilayer photographic materials, e. g. for colour photography, and such intermediate layers may be dyed or otherwise coloured so as to form filter or screen layers. Moreover, since such layers are readily soluble in ammonia solutions or in sodium carbonate solution they may form "stripping" layers permitting, on treatment with such solutions, the separation of the elements which they join together.

By selecting a metal alginate which is insoluble in the alkali usually present in developers but soluble in ammonia, it may be arranged that the elements of the multilayer assembly remain adhered together until such time as separation is required, when a simple treatment with ammonia solution will effect the separation. Many of the metal alginates form adhesive "stripping" layers which, though firm enough to prevent separation of the elements, joined together by their use when normally handled in the dry condition or when wet with water, are such that the elements can be pulled apart in the dry or wet condition, or under water, without damage to the elements.

The metal alginate layers of this invention may serve as adhesive "stripping" layers between various other layers, e. g. between a gelatin layer (for instance, a gelatin silver halide emulsion layer) on the one hand and a supporting cellulose film, cellulose acetate film, cellulose nitrate film or other cellulose derivate film or synthetic resin film on the other hand or between two gelatin layers or between a gelatin layer and a paper or glass support. The film element just described is illustrated in Figure 5 of the drawing wherein a support 21 has imposed thereon a layer 22 composed of a metal alginate of the above type which carries a gelatin silver emulsion layer 23. For the best results the metal alginate should be chosen with regard to the character of the layers which it is desired to join together.

An analogous type of film element is disclosed in Figure 6 of the drawing. It consists of a primary support 24 bearing a metal alginate layer 25 of the above described type on which is imposed a secondary support 26 which carries a silver halide emulsion layer 27.

The metal alginate layers of this invention may be dyed, pigmented or otherwise coloured

and may then serve as anti-halation layers removable at any desired stage after the exposure of the photographic element containing them. Thus such anti-halation layers may be coated on the side of the support opposite to that carrying a light-sensitive gelatino silver halide emulsion, or on the surface of such emulsion, the assembly may be exposed, and the antihalation layer removed (prior to, during or after development of the latent image) by any of the methods previously indicated, as desired.

Anti-halation layers according to this invention may conveniently consist of a dyed water-insoluble metal alginate layer, e. g. a calcium alginate layer, as a coating over a gelatin layer. An advantage of such an anti-halation layer assembly is that, since the dye is separated from the support layer by a gelatin layer, the tendency for the anti-halation dye to stain the support is eliminated or very much reduced. An alternative arrangement of anti-halation layer assembly is where the anti-halation dye is contained in the gelatin layer and the alginate layer is undyed; in this case the alginate layer will serve to hinder or prevent any de-sensitising action the anti-halation dye might otherwise have on the light-sensitive emulsion when in contact therewith, as in a rolled-up photographic film.

The following examples illustrate the invention but are not to be regarded as limiting it in any way:

Example I

In the production of a supercoating layer to avoid the formation of stress marks, the following composition is prepared:

Sodium alginate	grams	1.5
(Viscosity 200-400 centipoises estimated on a 1% solution in distilled water at 15° C.)		
Saponin	grams	2.0
Distilled water	litre	1

This solution is coated as a thin layer 1 on a gelatino-silver halide emulsion layer 2 carried on a paper support 3 and allowed to dry thereby forming the element described in Figure 1 of the drawing. It yields a layer, very satisfactory for its purpose, which disappears during processing thus providing silver prints suitable for the making of pigment prints in the bromoil and Carbro (registered trade-mark) processes.

Example II

For the same purpose as in Example I the following composition is prepared:

Sodium alginate	grams	6
(Viscosity 20-40 centipoises estimated on a 1% solution in distilled water at 15° C.)		
Saponin	gram	1
Distilled water	litre	1

This is coated directly on a gelatino-silver-halide emulsion carried on a support and allowed to dry. It yields a very satisfactory layer for the stated purpose.

The specific coating composition set forth in the above examples may also be employed to form alginate layers for any other of the purposes described above. Thus, with the addition of a dyestuff, e. g. Benzaurin (vide Schultz, Farbstoff-Tabellen No. 837) or Acid Green G (vide Colour Index No. 666) they may be employed to form filter layers or anti-halation layers.

Example III

A film 4 bearing a light-sensitive gelatin silver halide emulsion 5 is provided on the side opposite to that bearing the emulsion with a zinc alginate layer 6 formed by coating the film first with a 0.1-0.5% solution of zinc sulphate and then with a thin layer of an aqueous solution containing 2.5 gms. per litre of sodium alginate (viscosity 200-400 cp. estimated as a 1% solution in distilled water at 15° C.). The resulting element is described in Figure 2 of the drawing. This layer is dyed either by the inclusion of the dyestuff in the original sodium alginate solution or by subsequent treatment with a solution of the dyestuff. The dyestuff is selected with regard to the colour-sensitivity of the silver halide emulsion and suitable dyestuffs are Acid Magenta, Lissamine Green S. F., Soluble Blue A. S., Acid Green G and Ink Blue 8671. The dyed layer thus produced forms an excellent anti-halation layer and is removed on treatment with a dilute ammonia solution.

Example IV

A multilayer photographic sensitive material described in Figure 3 of the drawing is prepared, comprising a support 7 upon which are coated in succession

- (1) A gelatin layer 8
- (2) A layer 9 of sodium alginate (2.5 gms. per litre of sodium alginate, of viscosity 200/400 cp. estimated on a 1% solution in distilled water at 15° C.)
- (3) A layer 10 of collodion
- (4) A layer 11 of panchromatic emulsion
- (5) A layer 12 of sodium alginate as above, but containing a red dye
- (6) A layer 10' of collodion
- (7) A layer 13 of orthochromatic emulsion
- (8) A layer 14 of sodium alginate as above, but containing a yellow dye
- (9) A layer 10² of collodion, and finally
- (10) A layer 15 of non-colour sensitised emulsion,

layers (1), (4), (7) and (10) comprising gelatin from which the calcium salts normally present have not been removed. This material is exposed in the camera to a coloured scene, the last named emulsion layer facing the camera lens. The multi-layer material is then subjected to treatment with a solution of sodium carbonate whereby the three emulsion layers on their several collodion supports become separated from one another owing to the dissolution of the intervening alginate layers. The three image-bearing layers are then developed, washed, bleached in a reversal bleach bath such as an acidified solution of potassium dichromate, washed, uniformly exposed to light, and then individually re-developed in colour in known manner, i. e. the reversal positive image derived from the panchromatic emulsion is developed in a colour developer producing a blue-green dye image, that from the orthochromatic emulsion in a colour developer producing a magenta dye image, and that from the non-colour sensitised emulsion in a colour developer producing a yellow dye image. The coloured positive part images are finally reassembled in register to give a transparency in natural colours, or they may, if of suitable depth, be assembled upon a paper base to yield a paper print in natural colours.

Example V

Three positive part colour images are obtained from a set of three colour-separation negatives, by printing the latter upon photographic light-sensitive material described in Figure 4 consisting of a paper support 16 bearing (a) a layer 17 of gelatin soluble in warm water (b) a light-sensitive gelatino silver bromide emulsion layer 18 as is used in conventional development papers. After exposure, the three part-image prints are developed, fixed and washed in the usual way. The three part-image prints are then treated in a photographic bleach bath containing copper chloride and potassium dichromate in order to bleach the silver image and simultaneously tan the gelatin over the area of the silver image. The prints are then washed and immersed in a 4% aqueous solution of zinc sulphate, blotted free of surplus liquor, and squeezed each with its emulsion face in contact with a sheet of "Cellophane" 19 bearing a thin layer 20 of sodium alginate, preferably in the dry condition. The three "Cellophane" mounted prints thus obtained are allowed to dry and are then immersed in warm water, thus permitting their original paper supports to be removed, and leaving relief part images containing silver chloride adhered to the several "Cellophane" supports by intervening zinc alginate layers. These three silver chloride relief part images are now developed to colour in known manner, using coupling developers giving appropriate dye images. The three dyed positive part-colour images are then dried and assembled in superposition on a common final support, in the following manner:

The final support, which is preferably a paper support, is flooded with a 5% solution of gelatin and squeezed into contact with the first part-image layer on its "Cellophane" support (this may with advantage be the blue-green-processed part image derived from the original red-light record of the scene photographed). The assembly is dried and then immersed in a solution containing 5 cc. of ammonia water (S. G. 880) per 100 cc. of solution. After a minute or two the paper is peeled away from the "Cellophane" and now bears the first part image. This is rinsed free of surplus ammonia liquor, flooded with gelatin solution as before, and squeezed to the surface of the second "Cellophane" supported part-image layer (which may be the magenta-processed part image derived from the original green light record). The two part images are brought into proper register during this operation. The assembly is now dried and stripped from the "Cellophane" as before, and the operation repeated, bringing into position the third part image (which may be the yellow processed part image derived from the original blue-light record) stripping the assembly from the "Cellophane" and thus yielding a three-colour print on paper.

What we claim is:

1. A photographic element which comprises at least one support layer, at least one photographic silver halide emulsion layer and at least one layer of a metal alginate which is insoluble in water but soluble in a solution selected from the group consisting of ammonia solutions and dilute sodium carbonate solutions.

2. A photographic material which comprises a support layer, a layer of a light-sensitive gelatino silver halide emulsion and, between said layers, a layer of a metal alginate which is insoluble in water but soluble in a solution selected

from the group consisting of ammonia solutions and dilute sodium carbonate solutions.

3. A photographic material which comprises a support layer, a layer bearing a photographic image and, between said layers, a layer of a metal alginate which is insoluble in water but soluble in a solution selected from the group consisting of ammonia solutions and dilute sodium carbonate solutions.

4. A photographic material which comprises a support layer, a layer of a light-sensitive gelatino silver halide emulsion and, as a supercoat on said emulsion, a layer of a metal alginate which is insoluble in water but soluble in a solution selected from the group consisting of ammonia solutions and dilute sodium carbonate solutions.

5. A photographic material which comprises a support layer, a layer of a light-sensitive gelatino silver halide emulsion on one side of said support layer and, on the other side of said support layer, a layer of a metal alginate which is insoluble in water but soluble in a solution selected from the group consisting of ammonia solutions and dilute sodium carbonate solutions.

6. A photographic material which comprises a support layer, a layer of a light-sensitive gelatino silver halide emulsion on one side of said support layer and, on the other side of said support layer, a layer of a metal alginate which is insoluble in water but soluble in a solution selected from the group consisting of ammonia solution and dilute sodium carbonate solution,

said metal alginate layer containing an anti-halation colouring matter.

7. A photographic material which comprises a primary support layer, a secondary support layer, a light-sensitive silver halide emulsion inseparably attached to said secondary support layer and, between the primary support layer and the secondary support layer, a layer of a metal alginate which is insoluble in water but soluble in a solution selected from the group consisting of ammonia solutions and dilute sodium carbonate solutions.

8. A photographic multilayer material which comprises a plurality of units each comprising a support layer and a light-sensitive silver halide emulsion layer, said units being superposed on a primary support and adhered to each other and to the primary support by layers of a metal alginate which is insoluble in water but soluble in a solution selected from the group consisting of ammonia solutions and dilute sodium carbonate solutions.

9. In a process of photography involving the exposure and development of a photographic element which comprises at least one support layer, at least one photographic silver halide emulsion layer and at least one layer of a metal alginate which is insoluble in water and alkaline photographic developer solutions but soluble in aqueous ammonia solution, the step of removing said metal alginate layer by treatment with an aqueous ammonia solution.

LEONARD VINCENT CHILTON.
DUNCAN PAX WOOSLEY.