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LIGHT-SENSITIVE COATING AND THE METHOD FOR ITS PRODUCTION

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This invention relates to a coating composition, a method for its production and a light sensitive film produced therefrom, and to a dry mixture adapted for solution in dilute aqueous ammonium hydroxide to produce the coating composition. More particularly, it relates to a coating composition and to a light-sensitive film which is adapted for use in the production of photolithographic off-set printing plates.

Photo-lithographic off-set printing plates are usually of aluminum or zinc and have specially prepared surfaces, some areas of which are capable of accepting an ink having an oily vehicle and other areas which, when wet with water, will not accept ink. The area of the plates which accept ink form the printed image. Such plates must be constantly wet with water or an aqueous solution during the printing operation.

The initial step in the preparation of such a plate is a graining operation by which the surface of a metal plate is given a matte texture consisting of microscopic hills and valleys. This grained surface is then coated with a light-sensitive film and exposed through a negative of the image to be printed to an actinic light to produce a chemical reaction in the exposed portions of the film which renders them substantially insoluble in water. The unexposed portions of the film are then removed from the plate, leaving the light-hardened portions on the image areas of the plate to form its ink-receptive printing areas of the plate.

Casein is produced commercially by the treatment of milk with a mineral acid to cause the separation of the casein as curds from the whey of the milk. The whey is drained from the curds, which are then washed with water and dried. The dried casein is soluble in an aqueous solution of ammonia and is widely used in the form of an ammoniacal solution containing dissolved ammonium dichromate as a light-sensitive coating composition for the production of lithographic printing plates.

Photo-lithographic printing plates produced by the use of such light-sensitive coating are of limited durability, necessitating the preparation of duplicating plates for extended press runs. Furthermore, they do not reproduce half-tone images with the clarity achieved, for example, with plates made by photo-engraving processes. This relatively poor clarity is due to the matte texture of the grained surface underlying the image reproducing areas of the plate.

The preliminary graining of the metal has heretofore been absolutely essential in the preparation of photolithographic printing plates to obtain the selective wettability essential to this type of printing, by causing the non-image forming areas of the plate to retain more water than a smooth metal surface will retain. The quantity of water which is retained by this type of plate renders it unsuitable for the printing of surfaces which have a limited capacity for absorbing water, such as, for example, a cellulose acetate foil. Furthermore,

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the graining operation materially increases the cost of this type of printing.

The graining operation is a delicate one which, in present commercial practice is usually carried out by firms specializing in such work, rather than in the laboratories in which the plates are prepared for printing. It is an operation which must be repeated each time the metal plate is reused in the preparation of a printing plate. These factors require that the processing laboratories maintain a relatively large inventory of the plates to permit economy in the packing of used plates for regraining and require repeated trans-shipment of the plates. Further, each graining operation to which a plate is subjected removes metal from its surface, with the result that it can be regained only a limited number of times before it becomes useless due to rupture at its gripper edges. Each of the factors increases the cost of the printing operation.

Now, in accordance with this invention, I provide a coating composition which dries to a light-sensitive film from which image forming areas can be produced which are substantially more durable than those produced heretofore. My coating composition is suitable for use in the production of printing plates by the use of grained metal plates and is, in addition, suitable for the production of printing plates by the use of smooth, ungrained plates of a variety of different metals, including aluminum, zinc, tin plated steel, and stainless steel. Photolithographic off-set printing plates prepared by the use of ungrained metal plates by the use of my coating composition avoid the expense of the graining operation and are capable of reproducing half-tone images with a clarity which has been unobtainable by the use of printing plates having grained surfaces.

This invention is the result of research which has disclosed two facts. It has demonstrated that the treatment of an ammoniacal dispersion of casein, either in the presence or absence of dissolved ammonium dichromate, with an amount of a mineral acid insufficient to fully neutralize the ammonium hydroxide present in the solution, causes the separation of an organic material from the solution which appears to be a selective fraction of the casein itself.

This research has further demonstrated that the portion of the casein which remains in the ammoniacal solution, after the removal of the fraction which is separated by the acid treatment described above, is suitable for the production of a lithographic printing plate which is materially more durable and capable of producing a materially greater number of copies than one produced by the use of a casein which has not been subjected to the fractionation treatment.

The foregoing facts have led me to the conclusion that this acidic fractionation of the casein removes a portion thereof which tends to weaken the image on a lithographic printing plate in which it forms the major film-forming constituent. Conversely stated, the removal of this particular fraction, materially increases the durability of the image and, hence, the number of copies which can be produced by the use of the printing plate.

The coating composition, in accordance with this invention, comprises an ammoniacal solution of ammonium dichromate having dispersed therein milk casein from which a minor fraction has been removed by the addition of a concentrated mineral acid, to an ammoniacal solution of the casein in an amount less than the stoichiometric quantity necessary to completely neutralize the ammonium hydroxide present in the solution. In general, the fraction of the milk casein which has been removed by the treatment with a mineral acid is within the range of about 2%, by weight, to about 15%, by weight, of the casein originally present in the solu-

tion, and is preferably about 5%, by weight, thereof. Conversely stated, the casein fraction contained in this coating composition is about 98%, by weight, to about 85%, by weight, and, preferably about 95%, by weight, of a commercial milk casein. This coating composition preferably contains about one part of ammonium dichromate to about 8 parts of the acid fractionated casein.

In addition to ammonium dichromate, the acid-fractionated casein, ammonium hydroxide and water, this coating composition will normally contain the ammonium salt of the mineral acid which is utilized in the fractionation of the casein. Mineral acids which may be used for the fractionation of the casein are, for example, chromic acid and nitric acid. In general, I prefer to use chromic acid for the fractionation of the casein, since the residual salt left in the coating composition is an ammonium chromate or ammonium dichromate, i.e. the same salt which is present as the light-sensitizing agent in the ammoniacal coating composition.

By the method in accordance with this invention, for the production of my improved coating composition, I prepare an aqueous ammoniacal dispersion of milk casein and add thereto an amount of a concentrated mineral acid at least sufficient to cause the precipitation of a minor proportion of the dispersed milk casein, but less than the stoichiometric quantity required to neutralize all the ammonium hydroxide present in the solution, and thereby render it non-alkaline in reaction. I ordinarily use an amount of the mineral acid which will cause the precipitation of an amount of solids within the range of about 2% to about 15% by weight, and preferably about 5%, by weight, of the milk casein dispersed in the solution. I then remove the precipitated solids from the solution. After the precipitated solids are removed from the solution, I prefer to return the pH of the solution to substantially its original value, prior to the addition of the mineral acid, for example, pH 9.0, by the addition of concentrated ammonium hydroxide in amount to substantially replace that which has reacted with the mineral acid.

The other ingredients which I include in the completed composition may be added to the ammoniacal dispersion of milk casein either before or after the mineral acid treatment, although in practice I prefer to add them prior to the acid treatment. Thus, I prefer to prepare a composition which is, in effect, a prior art light-sensitive coating composition comprising essentially an aqueous ammoniacal solution of ammonium dichromate in which milk casein is dispersed and then subject it to treatment which a mineral acid and remove a precipitated fraction of the casein as described hereinbefore.

The ingredients which I add to the ammoniacal casein solution, either before or after the mineral acid treatment, essentially include ammonium dichromate. I may, in addition, include a minor amount of dispersed gelatin, for example, about 0.02%, by weight, of the solution and a small amount of a water-soluble organic dye, for example, an amount within the range of about 0.1% to about 0.3%, by weight, of the solution.

The light-sensitive film in accordance with this invention comprises a uniform molecular dispersion of ammonium dichromate in a film comprised essentially of milk casein, at least the milk casein component of which has been treated while dispersed in a dilute aqueous ammonium hydroxide solution to precipitate a minor fraction of the casein which is separated from the solution. My preferred film comprises about 12 parts, by weight, of ammonium dichromate for each 80 parts, by weight, of the fractionated casein. The film may also carry a molecular dispersion of a water-soluble dye, for example, an amount within the range of about one to about 4 parts, by weight, preferably about 2.5 parts, by weight, for each 80 parts of the fraction of milk casein present therein. The film may also contain a minor quantity of gelatin, for example, about 0.2 part, by weight,

for each 80 parts, by weight, of the said casein. It will also contain an ammonium salt formed as a by-product of the mineral acid treatment of the milk casein present.

The coating composition in accordance with this invention and all coating compositions heretofore used for the formation of light-sensitive films adapted for the production of photo-lithographic off-set printing plates are aqueous solutions having a relatively high water content, usually eighty percent or more of their total weight. They are corrosive in nature and are packaged in glass containers. These facts make the distribution of such coating compositions extremely expensive, when considered in terms of their actual content of film-forming solids which form the light-sensitive films.

In accordance with this invention I provide a dry mixture which is readily dispersible in a dilute aqueous solution of ammonium hydroxide to produce a coating composition which dries to a light-sensitive film adapted for the production of a photo-lithographic printing plate. This dry mixture comprises essentially ammonium dichromate and fractionated milk casein, in a uniform molecular dispersion in each particle of the solid. In addition to the ingredients mentioned, this solid mixture preferably contains a minor quantity of gelatin and a water-soluble, organic dye molecularly dispersed throughout each particle of the solid. I prefer to produce it in the form of a powder, from the standpoint of convenience in dispersing it in dilute aqueous ammonium to produce a coating composition. This dry powder, when dissolved in dilute aqueous ammonium hydroxide, produces the improved coating composition in accordance with this invention.

I produce this molecularly dispersed dry mixture by the evaporation of the ammonia and the water from the coating composition of this invention, leaving as a residue its content of fractionated milk casein, ammonium dichromate or ammonium chromate as the case may be, gelatine and eosin dye as a molecularly dispersed solid. In evaporating the ammonia and water from this solution I prefer to utilize an elevated temperature, but not in excess of 130° C. and preferably not in excess of 110° C. and to expose the solution to the higher temperatures for a minimum length of time, since a prolonged heating of the solution at the higher temperatures renders the dry powder partially insoluble in dilute aqueous ammonium hydroxide and therefore, unsuitable for my purpose. I have found that a double drum dryer heated by low pressure steam is satisfactory for carrying out this evaporation step.

As will be appreciated from the foregoing, to produce the dry, molecularly dispersed mixture of this invention, I first produce my improved light-sensitive coating composition, comprising essentially an aqueous, ammoniacal solution of ammonium dichromate or ammonium chromate and of fractionated casein, and then remove the water and ammonia therefrom under controlled conditions to produce a solid, preferably in finely-divided form, which is freely soluble in an aqueous solution of ammonia. The solution of this solid material in aqueous ammonia reconstitutes the original coating composition of this invention.

In preparing the coating composition in accordance with this invention, I find that it is desirable to prepare base solutions of its various ingredients and then prepare an intermediate mixture by mixing these base solutions. This procedure is convenient in practical operations, produces complete dispersion of each essential ingredient under the most favorable conditions and avoids adverse effects due to localized high concentration of individual ingredients in the mixing operations. Thus, I may utilize three base solutions in the preparation of my intermediate mixture. These base solutions are an ammoniacal solution of milk casein, an aqueous gelatin solution, and an ammoniacal solution of ammonium dichromate. I have

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found that it is advantageous to have the light-sensitive film formed from my finished coating composition colored to render it more readily visible. It may be colored with any water soluble, organic dye which is stable in aqueous ammoniacal solutions. I have found that it is convenient to add the dye to my intermediate mixture as a fourth base solution, although it may, if desired, be added as a final step in the completion of my coating composition.

A casein base solution which I have found convenient for use in the preparation of my coating compositions is shown by Example I.

Example I

Casein base solution:	Percent by weight
Milk casein -----	11.6
Ammonium hydroxide (27% NH ₃) -----	1.5
Water -----	86.9
	100.0

To prepare this base solution, I stir the milk casein into approximately three-quarters of the water content of the composition and mix for a period of about 40 minutes while raising its temperature to about 135° F. I then discontinue the heating of the mixture, add the ammonium hydroxide and continue the mixing for an additional period of about 45 minutes. I then add the remainder of the water to the composition and briefly continue the mixing to secure a uniform consistency. It is desirable to use a high quality milk casein in preparing this base solution. I have found that one sold under the trade name "Protovac" is suitable for my purpose.

A gelatin base solution for admixture with the foregoing casein base solution may, for example, have the composition shown by Example II.

Example II

Gelatin base solution:	Percent by weight
Gelatin -----	0.2
Water -----	99.8
	100.0

In the preparation of this base solution, I dissolve the gelatin in approximately 15% of the total water content of the solution, which has been heated to a temperature of about 150° F. and then allow this solution to stand until it has gelled. I then uniformly disperse this gel in the remainder of the water of the composition which is at a temperature of about 150° F.

An ammoniacal solution of ammonium dichromate, which may be termed a "sensitizing" base solution may, for example, have the composition shown by Example III.

Example III

Sensitizing base solution:	Percent by weight
Ammonium dichromate -----	7.86
Ammonium hydroxide (27% NH ₃) -----	17.21
Water -----	74.93
	100.00

This composition is prepared by merely mixing the components.

I have found that eosin is a suitable water soluble organic dye for use in my coating. A suitable base solution of eosin is illustrated by Example IV.

Example IV

Dye base solution:	Percent by weight
Eosin -----	4.3
Water -----	95.7
	100.0

To produce my intermediate mixture, I mix the base solutions illustrated by Examples I, II, III and IV in the volumetric proportions shown by Example V.

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Example V

Parts by volume

Casein base solution (Example I) -----	100
Gelatin base solution (Example II) -----	11
Sensitizing solution (Example III) -----	21
Dye base solution (Example IV) -----	8
	140

The admixture of these different base solutions as illustrated by Example V produces an intermediate solution having the approximate percentage composition shown by Example VI.

Example VI

Intermediate solution:	Percent by weight
Milk casein -----	8.28
Ammonium dichromate -----	1.18
Gelatin -----	0.016
Eosin dye -----	0.244
Ammonium hydroxide (27% NH ₃) -----	3.65
Water -----	86.63
	100.00

The solution illustrated by Example VI, although further treated as exemplified hereinafter to produce the improved coating composition in accordance with this invention, is itself a valuable coating composition and well suited for commercial use.

To produce the improved coating composition in accordance with this invention from the intermediate solution exemplified by Example VI, I add to this solution a concentrated mineral acid in an amount less than the stoichiometric quantity necessary to fully neutralize the ammonia present and then remove solid material which separates from the solution. Thus, for example, I may add an amount of concentrated nitric acid within the range of about 25 ml. to about 35 ml. and preferably about 30 ml. per gallon of solution. This addition of nitric acid causes the separation of a slimy, gelatinous precipitate from the solution which I believe to be a fraction of the milk casein originally dispersed therein. This precipitate is then removed from the solution by filtration. The pH of the intermediate solution exemplified by Example VI is about 9.0. The addition of 30 ml. of concentrated nitric acid (42° Baumé) reduces this pH slightly to about 8.8. After I remove the solid material which precipitates upon the addition of the nitric acid, I return the pH of the solution to its original value of about 9.0 by the addition of concentrated aqueous ammonium hydroxide.

The composition of the completed coating composition in accordance with this invention is illustrated by Example VII. This particular composition was produced by the addition of 30 ml. of concentrated nitric acid (42° Baumé) per gallon of an intermediate solution having the composition illustrated by Example VI followed by the separation of the precipitated solids and the readjustment of its pH to a value of 9.0 by the addition of concentrated ammonia.

Example VII

Coating composition:	Percent by weight
Nitric acid treated milk casein -----	7.91
Ammonium dichromate -----	1.17
Ammonium nitrate -----	0.92
Gelatin -----	0.016
Eosin dye -----	0.244
Ammonium hydroxide (27% NH ₃) -----	3.60
Water -----	86.14
	100.00

A comparison of Example VII with Example VI will show that the removal of the precipitate from the intermediate solution of Example VI has reduced the casein

content of the solution from 8.28% by weight, to 7.91%, by weight. Thus, the precipitation step removed 4.47% of the casein originally dispersed in the solution, in the case of this particular exemplification of my method.

Before using the coating composition illustrated by Example VII for the production of a photo-lithographic off-set printing plate, I dilute it with water. When using it to produce a light-sensitive film on an ungrained metal plate, I dilute it by the addition of an equal volume of water, thereby reducing its film-forming solids content by 50%. When using it to produce a light-sensitive film on a grained metal plate I reduce its film-forming solids content by 25% by the addition of water. These dilutions with water reduce the thickness of the light-sensitive film obtained by drying the composition, but does not alter its composition.

The composition of a light-sensitive film in accordance with this invention, produced by drying the coating composition exemplified by Example VII, regardless of the extent of its dilution with water is shown by Example VIII.

Example VIII

Light-sensitive film:	Percent by weight
Nitric acid treated casein -----	77.09
Ammonium dichromate -----	11.40
Ammonium nitrate -----	8.98
Gelatin -----	0.16
Eosin dye -----	2.37
	100.00

The light-sensitive film in accordance with this invention, for example, one of the composition shown by Example VIII can be used in the production of photo-lithographic printing plates on either smooth or grained metal plates of, for example, aluminum, zinc, tin plated steel, or stainless steel.

In the case of a smooth or grained metal plate of, for example, aluminum, zinc, tin plated steel, or stainless steel, I counter-etch the plate before depositing the light-sensitive film thereon. In the case of aluminum plates, I use a counter-etch of dilute acetic acid, for example, one containing 4 ounces by volume of glacial acetic acid per gallon of water. In the case of the other metals mentioned, I use a dilute solution of hydrochloric acid as a counter-etch. A solution containing 1 ounce, by volume, of concentrated hydrochloric acid per gallon of water is suitable.

In the case of smooth metal plates, I prefer to rub the counter-etched plate to a smooth satiny finish by the use of a composition containing mild abrasive, such as, for example, pumice powder, and follow this treatment by a second counter-etch. The satiny finish which I prefer to give the smooth metal plates is not to be confused with the grained surface which has heretofore been considered absolutely essential to the production of a satisfactory photo-lithographic off-set printing plate, since the extent of the abrasion involved in the two cases are of totally different orders of magnitude and of character.

I form the light-sensitive film, in accordance with this invention, on the metal plate by the usual procedure of pouring it on a plate being whirled in a horizontal plane and continuing the whirling until the film is dry.

The coating composition exemplified by Example VII may be dried to produce the molecularly dispersed dry mixture in accordance with this invention. The drying operation, may for example, be carried out as described hereinbefore. The composition resulting from the drying of the coating composition of Example VII is identical with that of the light-sensitive film shown by Example VIII.

To produce a coating composition for use in the production of photo-lithographic printing plates from this dry composition, I merely dissolve the composition in dilute aqueous ammonia. I may, for example, add 10

parts, by weight, of the solid to about 86 parts, by weight, of an aqueous solution of ammonium hydroxide containing 1%, by weight, of ammonia, and thereby produce a coating composition approximating that exemplified by Example VII. It may be dissolved in 172 parts of such a dilute solution of aqueous ammonium hydroxide to produce a coating composition ready for use on an ungrained metal plate or in 108 parts of such a dilute solution of ammonium hydroxide to produce a coating composition suitable for use on a grained metal plate.

In the foregoing, the various embodiments of this invention have been specifically exemplified by compositions in which a milk casein which has been fractionated by the use of nitric acid is used as the major film-forming constituent. Although nitric acid is one of the preferred mineral acids for use in the fractionation of casein in accordance with this invention, it will be understood from the foregoing that the other strong mineral acids are effective in the fractionation of casein, and that the use of casein fractionated by their use results in compositions which are definitely superior to the corresponding prior art compositions. In utilizing the strong mineral acids other than nitric acid, I substitute for the nitric acid used in the examples given hereinbefore, the stoichiometric equivalent of the particular mineral acid which I desire to use.

My research has demonstrated that the use of nitric acid for the fractionation of milk casein produces outstanding results, and that the compositions prepared by the use of the casein so fractionated are greatly superior to the prior art compositions. This research has also shown that chromic acid is even better than nitric acid for this purpose. It is at least as effective as nitric acid in the fractionation of milk casein to remove the fraction which weakens the image on a lithographic printing plate, and has the advantage of leaving as a residual salt ammonium chromate or ammonium dichromate, as the case may be, i.e. exactly the same salt which is added to the compositions to render them light-sensitive. As brought out hereinbefore, when nitric acid is used in my process, the final compositions contain residual ammonium nitrate resulting from the neutralization of the nitric acid by the ammonium hydroxide in the composition.

When using chromic acid as the fractionating acid, I may prepare a completed light-sensitive coating composition of the prior art type, add chromic acid thereto, remove a separated fraction of organic material therefrom and then readjust the pH of the composition by the addition of concentrated aqueous ammonia. Alternatively, I may prepare an ammoniacal solution of milk casein, fractionate it by the addition of chromic acid, readjust the pH of the solution by the addition of concentrated aqueous ammonia and then add ammonium dichromate and any other auxiliary ingredients which I desire in the final composition. Thus, I utilize chromic acid in exactly the same manner in which I utilize nitric acid or another of the strong mineral acids. Chromic acid is handled commercially in the form of chromic anhydride and I find that I can conveniently add chromic anhydride directly to the ammoniacal solution of milk casein in my method.

In utilizing chromic acid as the strong mineral acid in my method I may, for example, add three pounds of chromic anhydride to sixty-five gallons of the coating composition illustrated by Example VI. In carrying out this addition I find that it is desirable to agitate the coating composition solution in a manner which causes it to form a vortex, and pour the chromic anhydride into the vortex. After such addition of the chromic anhydride, soft lumps of organic material separate from the solution, which can be readily removed therefrom merely by straining the solution by passing it through a cloth.

The actual separation of a fraction of the casein in my method is clearly responsible for the improved properties of my compositions, rather than the presence of the

residual ammonium salt of the strong mineral acid present in the composition. My research has shown that a light-sensitive coating composition containing casein which has been fractionated with chromic acid, will produce a lithographic printing plate which will produce many more copies than a composition which is identical except in that it contains an unfractionated casein as its major film-forming constituent. Again, this research has shown that in the use of nitric acid as a fractionating acid, the fractionation of the casein is responsible for the increased durability of the lithographic printing plates made from the light-sensitive coating composition containing the fractionated casein, since the use of a light-sensitive coating composition utilizing ordinary milk casein to which an amount of ammonium nitrate equivalent to that produced by the neutralization of the nitric acid in my process and which is identical in composition to that containing the fractionated casein except as to its casein content, does not produce a lithographic printing plate having the greatly increased durability shown by the plates made by the use of the light-sensitive coating composition made with the fractionated casein.

In the foregoing, many details have been given as to the method and the products in accordance with this invention and both the method and the products have been specifically exemplified. It will be fully understood that the details and specific examples have been given for the purpose of fully disclosing my invention and that various modifications and changes can be made in these details without departing from the spirit of my invention or the scope of the appended claims.

This application is a continuation-in-part of my co-pending application Serial No. 470,118, filed November 19, 1954.

I claim:

1. A light-sensitive film adapted for use in the production of photolithographic off-set printing plates which comprises a molecular dispersion of ammonium dichromate in a film comprising essentially a milk casein which was originally produced by precipitation from milk and treated with nitric acid while uniformly dispersed in an ammoniacal aqueous solution and had a minor part precipitated and removed from the said solution.
2. A light-sensitive film adapted for use in the production of photolithographic off-set printing plates which comprises a molecular dispersion of ammonium dichromate and of a water soluble organic dye in a film comprising essentially a minor proportion of gelatin and a milk casein which was originally produced by precipitation from milk and has been treated with nitric acid while uniformly dispersed in an ammoniacal solution and had a minor part precipitated and removed from the said solution.
3. A light-sensitive film adapted for use in the production of photolithographic off-set printing plates which comprises a molecular dispersion of about 12 parts, by weight, of ammonium dichromate in a film comprising essentially about 80 parts, by weight, of a milk casein which was originally produced by precipitation from milk treated with nitric acid while uniformly dispersed in an ammoniacal aqueous solution and had a minor part precipitated and removed from the said solution.
4. A light-sensitive film adapted for use in the production of photolithographic off-set printing plates which comprises a molecular dispersion of about 12 parts, by weight, of ammonium dichromate in a film comprising essentially about 80 parts, by weight, of a milk casein which was originally produced by precipitation from milk treated with a strong mineral acid selected from the group consisting of nitric acid and chromic acid while uniformly dispersed in an ammoniacal aqueous solution and had a minor part precipitated and removed from the said solution.
5. A light-sensitive film adapted for use in the production of photolithographic printing plates which comprises

a molecular dispersion of about 12 parts, by weight, of ammonium dichromate in a film comprising essentially about 80 parts, by weight, of a milk casein which was originally produced by precipitation from milk treated with chromic acid while uniformly dispersed in an ammoniacal aqueous solution and had a minor part precipitated and removed from the said solution.

6. A light-sensitive film adapted for use in the production of photolithographic off-set printing plates which comprises a molecular dispersion of about 12 parts, by weight, of ammonium dichromate and a water soluble organic dye within the range of about 1 to about 4 parts, by weight, in a film comprising about 0.2 part, by weight, of gelatin and about 80 parts, by weight, of a milk casein which was originally produced by precipitation from milk and treated with nitric acid while uniformly dispersed in an ammoniacal aqueous solution and had a minor part precipitated and removed from the said solution.

7. A powdered solid adapted for solution in a dilute aqueous solution of ammonium hydroxide to produce a coating composition for use in the production of photolithographic printing plates, each particle of which comprises a molecular admixture of ammonium dichromate and a milk casein which was originally produced by precipitation from milk and treated with a strong mineral acid selected from the group consisting of nitric acid and chromic acid while uniformly dispersed in an ammoniacal aqueous solution and had a minor part precipitated and removed from the said solution.

8. A powdered solid adapted for solution in a dilute aqueous solution of ammonium hydroxide to produce a coating composition for use in the production of photolithographic off-set printing plates each particle of which comprises a molecular admixture of ammonium dichromate, and a milk casein which was originally produced by precipitation from milk and treated with nitric acid while uniformly dispersed in an ammoniacal aqueous solution and had a minor part precipitated and removed from the said solution.

9. A powdered solid adapted for solution in a dilute aqueous solution of ammonium hydroxide to produce a coating composition for use in the production of photolithographic printing plates, each particle of which comprises a molecular admixture of ammonium dichromate and a milk casein which was originally produced by precipitation from milk and treated with chromic acid while uniformly dispersed in an ammoniacal aqueous solution and had a minor part precipitated and removed from the said solution.

10. A powdered solid adapted for solution in a dilute aqueous solution of ammonium hydroxide to produce a coating composition for use in the production of photolithographic off-set printing plates, each particle of which comprises a molecular admixture of ammonium dichromate, a water soluble organic dye, a minor proportion of gelatin and a milk casein which has been treated with nitric acid while uniformly dispersed in an ammoniacal solution and had a minor part precipitated and removed from the said solution, the said molecular admixture being the product resulting from the removal of water and ammonia from an aqueous ammoniacal solution of the said ingredients of the said molecular admixture.

11. A powdered solid adapted for solution in a dilute aqueous solution of ammonium hydroxide to produce a coating composition for use in the production of photolithographic printing plates, each particle of which comprises a molecular admixture of ammonium dichromate, a water soluble organic dye, a minor proportion of gelatin and a milk casein which has been treated with a strong mineral acid selected from the group consisting of nitric acid and chromic acid while uniformly dispersed in an ammoniacal aqueous solution and had a minor part precipitated and removed from the said solution, the said molecular admixture being the product resulting

from the removal of water and ammonia from an aqueous ammoniacal solution of the said ingredients of the said molecular admixture.

12. A powdered solid adapted for solution in a dilute aqueous solution of ammonium hydroxide to produce a coating composition for use in the production of photolithographic printing plates, each particle of which comprises a molecular admixture of ammonium dichromate, a water soluble organic dye, a minor proportion of gelatin and a milk casein which has been treated with chromic acid while uniformly dispersed in an ammoniacal aqueous solution and had a minor part precipitated and removed from the said solution, the said molecular admixture being the product resulting from the removal of water and ammonia from an aqueous ammoniacal solution of the said ingredients of the said molecular admixture.

13. A powdered solid adapted for solution in a dilute aqueous solution of ammonium hydroxide to produce a coating composition for use in the production of photolithographic off-set printing plates, each particle of which comprises a molecular admixture of about 12 parts, by weight, of ammonium dichromate and about 80 parts, by weight, of a milk casein which was originally produced by precipitation from milk treated with nitric acid while uniformly dispersed in an ammoniacal aqueous solution and had a minor part precipitated and removed from the said solution, the said molecular admixture being the product resulting from the removal of water and ammonia from an aqueous ammoniacal solution of the said ingredients of the said molecular admixture.

14. A powdered solid adapted for solution in a dilute aqueous solution of ammonium hydroxide to produce a coating composition for use in the production of photolithographic off-set printing plates, each particle of which comprises a molecular admixture of about 12 parts, by weight, of ammonium dichromate and a water soluble organic dye within the range of about 1 to about 4 parts, by weight, in a film comprising about 0.2 part, by weight, of gelatin and about 80 parts, by weight, of a milk casein which was originally produced by precipitation from milk and treated with nitric acid while uniformly dispersed in an ammoniacal aqueous solution and had a minor part precipitated and removed from the said solution.

15. A method for the production of a coating composition adapted for use in the production of photolithographic off-set printing plates which comprises forming an ammoniacal aqueous solution comprising essentially milk casein and ammonium dichromate adding concentrated nitric acid thereto in an amount sufficient to cause the precipitation of a minor proportion of the dispersed milk casein but insufficient to render the said solution as a whole non-alkaline and separating the precipitated casein from the said solution.

16. A method for the production of a coating composition adapted for use in the production of photolithographic printing plates which comprises forming an ammoniacal aqueous solution comprising essentially milk casein and ammonium dichromate adding a concentrated strong mineral acid selected from the group consisting

of nitric acid and chromic acid thereto in an amount sufficient to cause the precipitation of a minor proportion of the dispersed milk casein but insufficient to render the said solution as a whole non-alkaline and separating the precipitated casein from the said solution.

17. A method for the production of a coating composition adapted for use in the production of photolithographic printing plates which comprises forming an ammoniacal aqueous solution comprising essentially milk casein and ammonium dichromate adding concentrated chromic anhydride thereto in an amount sufficient to cause the precipitation of a minor proportion of the dispersed milk casein but insufficient to render the said solution as a whole non-alkaline and separating the precipitated casein from the said solution.

18. A method for the production of a coating composition adapted for use in the production of photolithographic off-set printing plates which comprises forming an ammoniacal aqueous solution comprising essentially milk casein and ammonium dichromate adding concentrated nitric acid thereto in an amount sufficient to cause the precipitation of a minor proportion of the dispersed milk casein but insufficient to render the said solution as a whole non-alkaline separating the precipitated casein from the said solution and adding concentrated ammonium hydroxide to the said solution in an amount sufficient to substantially replace that which has reacted with the said nitric acid.

19. A method for the production of a coating composition adapted for use in the production of photolithographic printing plates which comprises forming an ammoniacal aqueous solution comprising essentially milk casein and ammonium dichromate adding concentrated strong mineral acid selected from the group consisting of nitric acid and chromic acid thereto in an amount sufficient to cause the precipitation of a minor proportion of the dispersed milk casein but insufficient to render the said solution as a whole non-alkaline, separating the precipitated casein from the said solution and adding concentrated ammonium hydroxide to the said solution in an amount sufficient to substantially replace that which has reacted with the said strong mineral acid.

20. A method for the production of a coating composition adapted for use in the production of photolithographic off-set printing plates which comprises forming an ammoniacal aqueous solution comprising essentially milk casein and ammonium dichromate adding concentrated nitric acid thereto in amount sufficient to cause the precipitation of about 2%, by weight, to about 15%, by weight, of the milk casein dispersed in the said solution, while leaving the said solution as a whole still alkaline separating the precipitated casein from the said solution and adding concentrated ammonium hydroxide to the solution in amount sufficient to substantially replace that which has reacted with the said nitric acid.

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