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CASEIN CONTACT PRINTING EMULSION

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This invention relates to a pigmented contact printing emulsion which is particularly adapted for use in reproducing multi-colored photographic images on flexible supports and especially vinyl plastic sheets.

As is known, multi-colored photographic images can be reproduced on flexible supports by coating the support with a light sensitive coating composition (usually containing a dichromate) which is dried and then subjected to light filtered through a negative. The light sensitive coating becomes hardened where it is exposed to light and the unhardened parts are then dissolved away leaving a positive of the negative. For multi-colored images a cycle of two, three, four or more coating compositions, each of which contains a pigment corresponding to one or more of the primary colors, are surprinted on the support.

With this type of coating composition, considerable difficulty has been experienced in reproducing half tones of the image and in getting the exposed portions of the composition to cling to the support. If excess pigment is used, or if a thick coating such as that employed for photographic relief images is applied to the support, hardening of the composition on exposure to light does not go right through to the support. As a result, the hardened portions wash off in development or rub off in use. On the other hand, when very small amounts of pigment are used, the image has a characteristic yellowish gray cast of hardened dichromate and its color is commercially unsatisfactory. An added problem occurs with vinyl plastic supports in that the plastic has a hydrophobic surface and it is virtually impossible to make the known water base coating compositions adhere to its surface.

In accordance with the present invention, these problems have been overcome and there has been produced an entirely satisfactory form of coating composition which tenaciously clings to flexible supports, especially vinyl plastic supports, and which faithfully reproduces the more delicate half-tones of the image. To this end, in my invention I provide a coating composition containing water, casein, a light sensitive water-soluble dichromate, preferably ammonium dichromate, an alkali such as ammonium hydroxide, and pigment.

In preparing my coating composition, I first make up a water dispersion of casein. The casein dispersion may be made by conventional means. One way in which the casein dispersion can be made is to take 1 part of casein, add 5 parts of water and soak for approximately one-half hour. Then alkali is added, preferably ammonium hydroxide, to adjust the pH of the mixture to a value above 7. Add additional water to adjust solid content of the mixture to about 7 to 9% by weight of casein and then agitate and heat the mixture to a temperature of about 140° to 160° F. and hold at that temperature for about 45 minutes. The temperature of the casein dispersion should not exceed 200° F., because casein starts to decompose at that temperature.

Water dispersions of casein are subject to microbial attack, and if the light sensitive coating composition is to be stored for any period of time, a preservative such as formaldehyde, or one of the proprietary preservatives now on the market such as Dowicide A (Dow Chemical Company), rosin amine, D acetate (Hercules Powder Company), or Vancide 51 LRT (Vanderbilt Co.), should be added in concentrations of about 0.5 to 1.0% based on the dry weight of casein.

Since the hardness of the exposed coating composition and its ability to adhere to the support depends in part upon the type of casein used, I prefer to use either an acid or rennet type of casein. I have achieved excellent results with a rennet type casein sold by the Borden Company under the name Protovac 401 and with an acid type casein sold by Hercules Powder Company under the name Paracase No. 7. Paracase No. 7 is an acid metallic caseinate. If an ordinary acid type casein is used, then one or more suitable hardeners, such as the water soluble salts of aluminum, chromium, or zinc, should be added to the casein in order to form a metallic caseinate which will give the required degree of hardness in the exposed portions of the coating on the support. In general, I use a metallic caseinate containing about 11¾% to 13% of water soluble salt based upon the dry weight of casein in solution. The term "acid metallic caseinate" is intended to mean those caseins which are precipitated from solution with an inorganic acid during manufacture and reacted with one or more of the above mentioned water-soluble salts to form a metallic caseinate.

Although any suitable alkali and water soluble dichromate, such as ammonium, potassium and sodium dichromate, may be used, I prefer to use ammonium dichromate and ammonium hydroxide. The dichromate, alkali and pigment may be added separately to the casein dispersion, but I prefer to make up an aqueous solution of the dichromate and then add it to the casein dispersion. The pH of the dichromate solution should be on the alkaline side. Preferably the pH should be about 8.5.

The pigment should be one which will readily disperse in water or one which can be made to disperse in water with the addition of suitable commercial dispersing agents. For best results, the pigment should also have good alkali resistance and it should not "bleed" in water. Finally, the particles of pigment should be in finely divided form and this can be readily achieved by grinding the pigment in water with standard pulverizing equipment such as a three-roller mill, colloid mills, etc., as is known in the art. The term "finely divided particles of pigment" is intended to mean a pigment having a particle size of less than approximately .0001 mm. in mean diameter. Such a product is readily available on the open market as a 20% dry pigment water dispersion, and I have achieved excellent results with the products made by Imperial Paper & Color Corporation. Examples of such products are:

Horicon yellow dispersion X–2439
Toluidine red disperesion X–2437
Monarch blue dispersion X–2446
Jet black dispersion X–2472
Malta red dispersion X–2355

After the dichromate and pigment have been mixed into the casein water dispersion, the pH of the mixture is adjusted with alkali to a value from approximately 8.5 to 10.5. If the pH is substantially below 8.5 the composition is sensitive to ordinary daylight and it cannot be stored for any period of time, and if the pH is above 10.5 the exposure time of the coating composition is increased, due to residual ammonia in the coating after it is dried on the support.

Finally, the entire mixture is subjected to a milling operation carried out at high velocity to disperse the solids and establish intimate contact between the casein and pigment. This is an important step in my process because the solid pigment particles and dichromate cannot be made to diffuse and become uniformly mixed through the casein colloid with ordinary hand milling or paddle type agitation, and if the coating composition contains agglomerates of pigment it will not adhere to the support where such agglomerates occur. I have achieved the required dispersion of pigment and dichromate by passing the composition through a micropulverizer as described in my copending United States patent application Serial No. 172,401, filed on July 7, 1950. However, other types of high velocity colloid mills are well known for fine grinding and mixing and such a mill may be employed provided it will mix the ingredients and produce a particle of the size produced with the micropulverizer of my copending application wherein the mixture in the chamber of the mill is rotated and hurled at high velocity and by centrifugal force against a milling surface until the solid particles in the mixture are ground fine enough to pass through slots positioned in a plate at the outlet of the mill. The slots in the plate in a satisfactory construction are about 0.01 inch wide. Because of the slope of the slots and the direction of rotation of the particles the size of particles coming from the outlet of the mill must be something less than 0.01 inch in shortest dimension. The term high velocity as used herein is intended to mean milling operations in which the impeller of the mill is driven at a velocity of the order of 14,000 R. P. M. or more. For best results the casein emulsion is repassed through the colloid mill for a total of two or three times to insure uniform distribution of the ingredients in relation to each other throughout the emulsion. I believe that when this milling operation is done the casein coats the pigment particles and holds them dispersed as discrete particles.

For best results I prefer to use a coating composition having the following approximate proportions of ingredients. In the examples the proportions are given as percentage by weight.

Ingredients:	Percent by weight
Casein	6.0 to 8.0
Water	82.0 to 91.8
Dichromate	2.0 to 4.0
Pigment (dry weight)	0.2 to 6.0
Specific gravity	1.020 to 1.045
pH	8.5 to 10.5

I have found it highly important to keep the specific gravity and the amount of pigment in the coating composition within the specified limits in order to faithfully reproduce half-tones and achieve the proper bond with the support. Otherwise, the proportions of ingredients may be varied by plus or minus 50% depending upon the intended use for the composition. The specific gravity of the composition can be readily adjusted by changing the proportion of water and casein provided the amount of pigment is kept within the specified range.

Adherence to the support depends primarily upon the penetration of light which should reach through to the molecules of the coating on the surface of the support. If the amount of pigment exceeds the top limit specified, it will interfere with transmission of light and the exposed portions of the coating will not then give the desired adhesion, and any increase of dichromate will not help to give a better bond. If the amount of pigment is below the amount specified, the image has a yellowish-gray cast of the exposed dichromate, and reproduction of half-tones and color is poor. Within the range of pigment specified, the specified amount of dichromate is highly effective for converting the exposed portions of the coating into insoluble form. Further, the amount of pigment used in the mixture is readily held in suspension by the casein dispersion.

Although my coating composition is particularly adapted for use with sheeted plastic material, especially vinyl plastic sheets, it will be understood that I do not intend to limit my invention to such plastic materials and I have used my coating composition on such supports as paper, chipboard, tracing cloth, glass, Plexiglas and dinoglass. If desired the support may be given a grained surface which tends to increase the bond, but this is not essential, and my coating composition gives a good bond with supports having a smooth surface.

I have had particularly good results with the following composition on vinyl plastic sheets, Plexiglas, glass, Lucite and dinoglass.

Ingredients:	Per cent by weight
Rennet casein	7.6
Water	87.5
Ammonium dichromate	3.4
Pigment (dry weight)	1.5
Specific gravity	1.030
pH	9.0

Substantially the same results were achieved by substituting an acid metallic caseinate for the rennet casein and by substituting either sodium or potassium dichromate for the ammonium dichromate in the specified proportions.

A preferred method for using my coating composition is illustrated in the following example. It will, however, be understood that this example is only by way of illustration and it is not intended to impose any limitations upon the way in which my composition may be used.

A vinyl plastic sheet is cleaned with a dilute ammonia solution containing approximately 1 ounce of 28% ammonia in 1 gallon of water. The sheet is placed in a conventional whirler and rotated at a speed of approximately 65 to 75 R. P. M. A thin coating of my casein coating composition for vinyl plastic sheets is then applied by pouring the composition on the sheet. After the sheet is coated, it is whirled for about 10 minutes to dry the coating. During the drying operation, alkali is evaporated and this reduces the pH of the coating composition so that it is sensitive to actinic rays of light. The sheet is then placed in a vacuum frame and exposed to the light of a carbon arc lamp filtered through a negative of the image. The light reduces the chromate to an insoluble complex chromate ion which in turn converts the casein into a water-insoluble form. In general, the coating is exposed for about 5 minutes.

The sheet is then developed by placing it in a weak ammonia solution (approximately 1 ounce of 28% ammonia to 1 gallon of water) to wash off the unexposed portions of the coating, leaving a positive of the negative or a negative when the original image is in the form of a positive mask. This development of the coating takes about 2 minutes. If the image is to be multicolored, the same procedure is repeated until all the necessary colors have been surprinted on the support. If desired my coating composition may be applied to the support in a thin coat by spraying it on. However I prefer to use a whirler which insures that each layer will have uniform thickness.

The resulting hardened image is insoluble in water and it has excellent resistance to acids and alkali. The image will not rub off in use and in fact the only satisfactory way to remove it is to scrape it off with sharp abrasives. Reproduction of half-tones is exceptionally good, so that my reproductions may be used for "proving" in lithographic printing operations. The great convenience of my composition is that the plastic proving plates may be processed in about 20 minutes per color, whereas the ordinary metal proving plates require expensive equipment and up to 3 to 5 hours per color.

Multicolor images made with my coating composition

on vinyl plastic sheets have exceptionally good dimensional stability and are particularly good for proving in the map making field. In this connection, it will be noted that for some purposes it is desirable to reverse the field of color. In such case the coating composition is exposed to light filtered through a positive print of the image which gives a negative of the positive.

In some special cases my coating composition, because of its ability to adhere to smooth surfaces, may be used to advantage on metal plates, for example, in lithographic printing operations. In such case, the composition is used without pigment and upon exposure to actinic rays of light it provides a hard, glossy surface coating which is easily wet with ink. I prefer to use a coating composition having the following proportion of ingredients for metal plates:

Ingredients:	Percent by weight
Casein	3.9
Water	79.0
Dichromate	10.5
Ammonium hydroxide	6.6
Specific gravity	1.01–1.04
pH	8.4–9.8

It is to be noted that this composition is prepared as described above for my pigmented coating composition except that the final milling operation is not required.

Further, it will be understood that it is intended to cover all changes and modifications of the preferred form of my invention herein chosen for the purpose of illustration which do not constitute departures from the spirit and scope of my invention.

What I claim is:

1. The method of preparing a contact printing emulsion adapted to be retained on plastic and glass surfaces which comprises the steps of dispersing a casein selected from the group consisting of rennet and acid metallic caseinates in an alkaline aqueous medium having a pH above 7, adding solid pigment particles and a water soluble light sensitive dichromate to the casein water dispersion, the pigment being added in amount sufficient to bring the pigment content of the resulting mixture within the range of about 0.2% to 6.0% by weight of the mixture and the dichromate being added in amount sufficient to bring the dichromate content of the resulting mixture within the range of about 2.0% to 4.0% by weight of mixture, adding alkali to bring the pH of the mixture within the range of about 8.5 to 10.5, adjusting the water and casein content of the mixture to bring the specific gravity of the final mixture within the range of about 1.020 to 1.045, and then delivering the final mixture into the chamber of a colloid mill, rotating the mixture in such chamber at a velocity of about at least 14,000 R. P. M. to grind the solid particles and uniformly disperse the ingredients throughout the mixture and continuing such grinding and dispersing operation for a given particle of solid until the particle is reduced in size to give a mixture with particles the shortest dimension of which is less than 0.01 inch and to emulsify and uniformly disperse the ingredients in relation to each other throughout the resulting casein emulsion whereby the emulsion upon exposure to light will adhere to a flexible sheet, such as a vinyl plastic sheet, in a substantially continuous film even after repeated flexing of the sheet, and whereby the half-tone colors of an image may be faithfully reproduced by applying and exposing successive coatings of the casein emulsion containing different primary pigment colors.

2. The contact printing emulsion produced by the process of claim 1.

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