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PROCESS FOR HARDENING COLLOIDS

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In the application of colloids, such as casein, gelatine, agar-agar, gum arabic or the like in industry, it is frequently necessary to harden them and for this purpose there are used in general materials like alum, aldehyde, quinone, tannin and other tanning materials, in short, substances which in a single operation harden colloids or make them insoluble.

Another hardening procedure, which is adopted for example in the art of printing, consists in subjecting a bichromatized colloid layer, such as a gelatine layer, to the action of light. As is well known, bichromates are chromium salts which do not harden gelatine. It is only by the action of light that the bichromate undergoes a change, as the result of which chromic salts are produced which exert a hardening action on gelatine. If while being exposed to light the bichromatized colloid layer is shielded by a photographic negative having a silver deposit of varying density, the amount of chromic salts produced in the colloid layer varies in an inverse proportion to the densities of the negative. Thus by the varying amounts of chromic salts a picture composed of differently hardened areas is produced on the colloid layer (collotype and pigment processes). According to the present invention the action of chemicals having a similar effect is made use of instead of the action of light.

As is well known to those skilled in the art, gelatine layers which have been treated with a hardening agent, such as formaldehyde, chrome-alum or the like, present a very great inconvenience, because in the course of time they undergo a further hardening, which is undesirable and which is caused by storage conditions and the like and which cannot be prevented nor controlled. By this further hardening the properties of the stock are changed in such a manner that it is no longer suitable for the particular purpose for which it is intended, as for example, the production of a relief by swelling. The present invention relates to a new method of hardening which overcomes this inconvenience. Since it is not advantageous to harden the colloid prior to storage due to the further hardening described above and since customers do not like to perform the entire hardening operation themselves immediately before use, the hardening procedure is divided into two operations according to the present invention. The first operation, which may be called a preparatory one, is carried out during the fabrication of the colloid, while the second operation, the hardening operation properly so-called, is carried out only immediately before use. Between these two operations there may be a considerable lapse of time. The first operation consists in incorporating with the colloid substances which are not hardening agents per se but which produce hardening agents by a reaction with other substances which also are not hardening agents per se and which are added to the colloid in the second operation.

Thus the essential features of the present invention are:

1. The hardening of the colloid by a hardening agent produced in or on the colloid by the reaction of two substances each of which is not a hardening agent per se and which are not incorporated with the colloid simultaneously but at different times in separate operations;

2. The hardening of the colloid in two separate operations in which the lapse of time between the two operations may be of any length desired and of which operations only the second one initiates the hardening.

It has already been proposed heretofore to harden colloids by incorporating in them two substances which by reaction form a hardening agent, but these substances were added at once and together, the hardening thus being produced immediately during the fabrication of the colloid mass. A hardening process like that of the present invention, in which the two substances are added at different times so that the hardening may be initiated at any desired time, has not been disclosed heretofore.

The hardening can be controlled in any desired manner by varying the proportions of material originally added. For example, there may be added to a gelatine layer a suitable reducing agent which does not of itself

harden the gelatine and when the layer is to be further treated it may be introduced into a bath consisting of a solution of an oxidizing agent, so selected that by reaction with the reducing agent hardening substances are formed.

This process is useful in many arts, among others in the treatment of spun threads, in the production of films from plastic masses, in the art of reproduction.

In order to improve the adhesion of the colloid printing layer on its support (glass, paper, celluloid or the like) it has been proposed in the graphic art to subject the layer sensitized with bichromate to a short exposure to diffused light through the support and then to perform the usual copying operation. In particular this is said to be necessary in making colloid printing layers on a celluloid support, since the known methods of fixing a gelatine layer on celluloid do not suffice in view of the mechanical requirements arising from the use of the printing-press and a general illumination of the sensitized layer through the celluloid appears unconditionally necessary. This general illumination from the back has, in addition to the trouble it involves, the disadvantage that it affects the character of a picture in an uncertain and uncontrollable manner, according to the degree of the action of the light, the transparency of the support, the thickness of the layer and the like. If in consequence of inattention the illumination is protracted, the copy may be completely ruined. If there be particles of dirt or spots of dried sensitizing agent (for example bichromate, which now acts as a yellow filter for light) on the back of the support, the printing layer comes away from the support layer at those places which have not been sufficiently illuminated. In many cases illumination from the back is precluded, for instance in the case of opaque supports (metal), supports which are not uniformly translucent (paper of strong structure), or when the support has matter on its back which makes it opaque. The chemical process in this illumination through the back consists in a gradual and continuous strong hardening of the part of the sensitized layer which is adjacent to the support, so that for the further treatment of the printing plate the layer is damaged in respect of its capacity for swelling and as a consequence it adheres to the support.

When it is attempted to substitute for the back illumination a hardened intermediate layer on which the main layer is afterwards formed or deposited, the two layers do not unite together. When, however, the intermediate layer is hardened in the manner which forms the subject matter of this invention it causes the two layers to adhere firmly together in consequence of certain diffusion phenomena.

It is also possible to harden the whole of the printing layer according to the invention. If the hardening does not extend over the whole surface of the printing layer but is locally limited, a cliché may be obtained directly fit for flat printing processes. If, however, the unhardened colloid is washed away the cliché may be used for relief printing. Having produced by the new process a hardened colloid relief on a metal support and having removed the unhardened colloid the metal may be etched in order to obtain for instance a cliché for intaglio printing.

The following examples without limiting the invention illustrate how the process can be performed. Of course, the particulars may be varied within wide limits, any suitable colloid in any suitable form being employed as well as other hardening agents formed by reacting with non-hardening substances of any kind of non-hardening substances of any kind previously incorporated into the colloid.

I am aware that it has already been proposed to incorporate into gelatine bichromates of ammonium or of potash, which do not immediately exert a hardening action on gelatine. However, it is well known to those skilled in the art that bichromatized gelatine undergoes an undesired hardening within a few days due to a slow decomposition of the bichromate salt occurring without any influence of other substances or of light. Hence I do not contemplate the use of bichromate as a substance to be uniformly distributed in a colloid and to be acted upon later by another substance to produce a hardening agent. Bichromates may, however, be applied in my process as second substance which, to produce an immediate hardening agent, is added to a colloid containing in uniform distribution a substance not capable of hardening the colloid by itself. This especial application of bichromate salts has not been suggested heretofore.

The present invention comprises in general adding to a colloid, such as gelatine, a substance which will not of itself harden the colloid even on standing, but which is capable of reacting with a second substance, incapable of immediately hardening the colloid, to form a substance which is capable of immediately hardening the colloid.

Example 1.—A 10% solution of gelatine containing ferro-ammonium sulphate (1% calculated on the dry weight of the gelatine) is spread on a suitable support and dried. When it is immersed in a bath consisting of 3 grams of potassium bichromate dissolved in 100 grams of water there is immediate formation of ferric salt and chrome compound both of which give rise to a controlled hardening of the gelatine layer.

Example 2.—On celluloid there is spread a liquid which contains one per cent of hydroquinone in addition to the usual solvents for celluloid and gelatine. When the layer has been dried it is coated with a solution of gelatine. When the gelatine layer is sensitized with potassium bichromate as recited above there is produced between the materials used a reaction, the consequence of which is a firm adhesion of the printing layer to the celluloid.

Example 3.—There is spread on a celluloid film, prepared as usual, a layer a few thousands of a millimeter thick of gelatine containing 2 per cent of formaldehyde bisulphite. When the layer has been dried there is poured upon it the usual printing layer suitable for a photomechanical process. When this printing layer is dry it is treated with a 5 per cent solution of alkali whereby the formaldehyde bisulphite is decomposed and the liberated formaldehyde hardens the intermediate layer, so that there is an adequate adhesion of the printing layer in use in printing.

Example 4.—A gelatine solution is mixed with 2 per cent of hydroquinone and is allowed to set in any form, for instance as a thin layer, and dried. When the layer is treated with potassium bichromate as recited above throughout its mass or locally, for instance in written character, there is an instantaneous formation of quinone and chrome compound and consequently a hardening of the gelatine at the places treated. If, for instance, writing is produced in this manner by stamping on a gelatine layer this layer may afterwards be used in known manner for printing according to the usual photographic printing processes. The gelatine layer necessary for such a process may vary in its thickness between wide limits.

Example 5.—A web of animal or vegetable fibres or of artificial fibres (paper or the like) is saturated with a gelatine solution containing 5 per cent of formaldehyde-sulfoxylate it is afterwards immersed in a 5 per cent bath of potassium bichromate whereupon the gelatine is immediately hardened and the web is permanently impregnated therewith.

It is of course understood that the invention is not limited in any way to the specific materials, manipulations or proportions recited in the preceding examples.

Having now described my invention what I claim is,—

1. The process which comprises treating with a solution of an alkali a gelatine layer containing formaldehyde bisulfite.

2. As a composition of matter, a gelatine layer containing formaldehyde bisulfite.

In testimony whereof I affix my signature.

ALFRED MILLER.