Patented Jan. 30, 1945

2,368,516

UNITED STATES PATENT OFFICE

2,368,516

HECTOGRAPH COMPOSITIONS AND BLANKETS

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No Drawing. Application July 28, 1941, Serial No. 404,385

3 Claims. (Cl. 35—6)

The invention relates to hectograph compositions and hectograph blankets and method of preparing same.

A principal object of the invention is the provision of a substantially non-ageing hectograph mass of high mechanical resistance.

Another object is to provide a quick and economical method for preparing a hectograph blanket having a copy mass of stable hardness.

Hectograph compositions comprise a gel forming material such as glue or gelatin, a dispersing medium such as water or an aqueous solution of some relatively non-volatile hygroscopic material such as glycerin or invert sugar; and a tanning agent such as formaldehyde, chrome alum, or the like. A suitable commercial composition may contain glue or gelatin 30 parts by weight, water 45 parts by weight, glycerin 300 parts, and formaldehyde .13 part by weight. The mixture is heated and agitated to form a sol and the sol is coated on a flexible backing such as paper or cloth and allowed to cool and form a gel. The backing containing a layer of gel is stored and allowed to age for several weeks, during which time the tanning agent combines with the gelatin to increase the toughness and heat resistance of the mass to the point where the mass is suitable for use in commercial hectograph machines.

It is well known that when tanning agents are used in quantities sufficient to impart to the hectograph mass the necessary degrees of mechanical resistance that the tanning agents tend to continue the tanning action so as to cause an excessive hardening of the copy mass, finally rendering it brittle and useless.

Most hectograph compositions have a pH below 7.0 due to the fact that most of the commercial glues are on the acid side.

In an acid medium, many tanning agents such as the aldehydes and ketones have a slow and often negligible tanning action on gelatin, particularly when used in small amounts.

It is known that the tanning action of aldehydes will be increased by using an alkaline medium, and hectograph compositions have been prepared based on this phenomenon, but so far as I know, no one has carried out tanning of hectograph masses in an alkaline medium or at some predetermined pH, and then stopped the tanning action at a predetermined point by shifting the pH to an acid level or some pH at which tanning will practically not take place.

I have discovered that after a hectograph composition is made alkaline by means of a volatile alkaline agent such as, for example, ammonia, methylamine, or the like, then the pH will remain on the alkaline side for a period of time, depending upon the quantity of alkali used, and will then drift back to a neutral or acid condition. As a result, a tanning agent which is active in an alkaline medium only will exert its tanning action in such a composition only while the composition remains alkaline, and will become inactive when the pH has drifted back to the neutral or acid side whereby further progressive tanning is prevented.

The shift in pH is due at least in considerable part to an evaporation of the volatile alkali. This is shown by the fact that I can use larger quantities of aldehyde than used in the Nielsen process described in Patent 1,938,927 and thus bring the copy mass to the desired degree of hardness in a much shorter length of time than Nielsen, and also obtain a stable hardness and melting point in a shorter period of time.

In carrying out this invention, I may use any tanning agent which is active at a certain pH, and which becomes inactive at a lower pH. The lower pH at which the tanning agent becomes relatively inactive does not necessarily have to be at a pH of 7 or below but preferably it is.

The preferred tanning agent is one which is highly active at some pH above 7 and which is practically inactive at some pH below 7. Tanning agents of this type include the quinones. One of the most suitable quinones is ordinary quinone, namely, parabenzoquinone. Other suitable quinones includes the orthobenzoquinones and the toluoquinones and xyloquinones.

The aldehydes such as formaldehyde and acetaldehyde may be used, but greater care must be taken in regulating the amounts of these agents so that they give suitable tanning action in an alkaline medium but substantially no tanning action in an acid medium. If too large quantities of aldehydes are used, the rate of reaction in an acid medium is not satisfactorily decreased and an excessive hardening of the hectograph mass may take place during commercial use. On the other hand, if the quantities of aldehydes used are too small, it will take longer to satisfactorily tan the hectograph mass in an alkaline medium. With the quinones, the difference between the rate of reaction in an alkaline medium and an acid medium is much greater than for the aldehydes, and therefore the quantities of the quinones is of much lesser importance.

To more clearly set forth the practice in accordance with the invention and to more specifically point out the nature of the product and

process contemplates thereby, several specific, illustrative examples are hereinafter set forth, it being understood that these examples illustrate several embodiments which have given satisfactory results and are not intended to restrict the invention thereto.

Example I

	Gms.
Gelatin (pH below 7.0)	180
Water	270
Glycerin	1,700
Quinone dissolved in suitable solvent (e. g., ethyl alcohol, acetone)	.4

Mix, and add 7 cc. 28% ammonium hydroxide.

Example II

	Gms.
Glue (pH below 7.0)	200
Water	270
Glycerin	1,500
Quinone in suitable solvent	.35

Mix, and add 7 cc. 28% ammonium hydroxide.

In these examples, the ammonia brings the pH of the composition to about nine, at which point quinone is a highly effective tanning agent. The hectograph composition is poured in the usual manner onto a backing prepared as well known in the art.

On examination, it was found that within one week the pH of the mass had changed to seven and that in three weeks the pH had changed to 5.3, at which pH no further tanning was found to take place. The compositions prepared in this manner have been tanned to a degree exceeding that to which they could be tanned by any other procedure known, without causing progressive hardening; such progressive hardening being prevented by the change in pH described above.

In the preferred method of practicing the invention the tanning agent is allowed to act on the gelatin composition for some time before the alkalizing agent is added. When this procedure was followed, the resulting compositions had a softening point about five degrees centigrade higher than if the alkalizing agent and the tanner were added simultaneously. Also the masses prepared in accordance with this process, showed more satisfactory hydrothermal properties and a wider range of tolerance to moisture treatment.

While I do not wish to commit myself to any theory regarding the cause of this desirable result, I believe that by allowing the tanning agent to act on the glue or gelatin at a pH range where the tanner is ineffective for preferably at least twenty minutes, the tanning agent penetrates into the gelatin molecule system beyond the shell of hydration of the molecules thereby securing, so to speak, a hold of the inner parts of the gelatin molecules in a manner which could not have been achieved if the initial action between the tanning agent and the protein had been at a pH where immediate tanning would have followed.

In particular, when parabenzoquinone or the like is used as the tanning agent, and ammonia, or an amine is used as the alkalizing agent, simultaneous admixture of the quinone and the amine leads to the formation of aromatic amines or similar less potent tanning or non-tanning reaction products. Thus, a substantial part of the quinone is transformed into non-tanning substances, before it has reacted with the protein.

If the quinone is added before the ammonia, it reacts practically quantitatively with the protein; and the tanning which takes place upon the subsequent addition of ammonia utilizes more completely the tanning potential of the quinone.

The following examples illustrate this form of the invention:

Example III

	Parts by weight
Gelatin (200 Bloom) (pH below 7.0)	100
Water	150
Glycerin	1400
Parabenzoquinone	0.200

Dissolved in suitable solvent (e. g., acetone).

The gelatin was allowed to swell in the water for one hour and then melted at 60° C. The glycerin was heated to 70° C., the quinone solution added with stirring, and the mixture incorporated with the molten gelatin. The mix was held at 50 to 55° C. for one and one-half hours.

Five parts by weight of 28% ammonium hydroxide weer added with stirring, and the composition was poured onto a backing sheet coated with a lacquer containing ten per cent of naphthenic acid. The resulting hectograph films were tested and found satisfactory in all regards.

Example IV

	Parts by weight
Gelatin (pH below 7.0)	100
Water	150
Glycerin	1400
Quinone in acetone	.150

The same procedure is followed as in Example III excepting the mix is held at 50 to 55° C. for two hours. Ten parts by weight of tetraethanol-ammonium hydroxide (40% solution) was then added with stirring, the hectograph films prepared and tested as in Example III.

It was found that the shift in pH from an alkaline to an acid reaction took place with tetraethanol ammonium hydroxide in substantially the same way as when ammonia was added as the alkalizing agent. In this case the shift in alkalinity may have been due to a slowly proceeding decomposition of the alkalizing agent.

While in these instances tanning agents have been employed, which are active at an alkaline pH, and substantially inactive under acid conditions, it is manifest that the principle of the invention is equally applicable to tanning agents which are highly active at an acid pH, and substantially inactive at a more alkaline or a neutral reaction. Such tanning agents are for example most vegetabilic tanning extracts, tannic acid, and the like. The pH of the roll may be adjusted to the optimum acidity for the action of such tanning agents by the incorporation of small amounts of volatile acids, such as formic acid, acetic acid, or the like. Even a non-volatile acid such as malic or phosphoric acid may be employed, in which event the pH may be brought back to the neutral or alkaline state by applying to the surface of the roll an acid neutralizing agent, such as, e. g., sodium carbonate or ammonia.

Also, when tanning agents active in the alkaline range are employed, acidification of the mass can be caused by applying to the surface of the roll an acidifying solution, such as for example dilute acetic acid, orthophosphoric acid, citric acid, or the like.

It is thus apparent that the invention is capable of wide variations in its applications. The examples given by way of illustration show embodiments which have been found most practical,

but useful results may be readily produced by other procedures, such as for example those just outlined. The invention broadly contemplates the idea of employing a tanning or hardening agent active at a certain pH and inactive at another pH, maintaining the composition at the pH where the tanning agent acts energetically, and then causing or allowing the pH of the mass to change to a point where tanning substantially ceases.

While there have been shown and described certain embodiments of the invention, it is to be understood that it is capable of many modifications. Changes, therefore, may be made without departing from the spirit and scope of the invention as described in the appended claims, in which it is the intention to claim all novelty inherent in the invention as broadly as possible, in view of the prior art.

I claim:

1. The method of preparing a hectograph blanket having a stabilized copy surface which comprises coating a backing with a gel forming composition comprising gelatin, a quinone, and a volatile alkali in sufficient amount to effect substantial tanning before said alkali is reduced by volatilization to an amount at which tanning is stopped.

2. In the method of preparing a hectograph blanket having a stabilized copy surface, the steps which comprise forming a molten non-alkaline composition comprising gelatine, water and a quinone, maintaining said composition in the non-alkaline condition for a substantial period of time, and then adding a volatile alkali to bring the composition to an alkaline state.

3. In the method of preparing a hectograph blanket having a stabilized copy surface, the steps which comprise forming a molten non-alkaline composition comprising gelatine, water and a quinone; maintaining said composition in the non-alkaline condition for a substantial period of time, and then adding a volatile amine to bring the composition to an alkaline state.

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