

UNITED STATES PATENT OFFICE

2,116,536

CELLULOSE COMPOSITION MATERIALS

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No Drawing. Application August 27, 1931,
Serial No. 559,778

7 Claims. (Cl. 106—37)

This invention relates to an improved plasticizable mixture which is initially moldable, which is especially adapted to take fine imprints and impressions from copy plates and reliefs, and when hardened or solidified into a film or sheet, is serviceable in the printing, graphic and reproduction arts as a printing plate having printing impressions in the surface thereof.

The plastic material which I have invented possesses such characteristics as make it especially valuable for use in the printing, graphic and reproduction arts. My finished product herein disclosed will take a sharp, clear and accurate impression of surfaces, such as copy reliefs, when the composition is pressed forcibly into contact therewith and allowed to harden and set. In addition, the product does not shrink upon hardening or with age, is free from "plastic flow", is substantially non-thermoplastic and accurately and uniformly retains its original surface shape and contour. The product as herein disclosed will not adhere to a dampened or water swollen gelatine copy relief, and, therefore, constitutes an excellent material for printing plates which can be cast from such a copy relief. When fully solidified, the improved product of the present invention is hard, tough, durable and wear resisting and is especially useful and valuable in situations where such a material is desired.

The printing plates are made and cast from my improved composition substantially as follows: Using the screens and photographic apparatus customary in the printing industry, a positive (if intaglio), or negative (if half tone or relief) is taken on a gelatine plate (generally backed with celluloid) impregnated with a chromate salt. Where the light strikes the gelatine it is rendered nearly unswellable by water. The exposed gelatine plate is moistened with water (by immersion or otherwise) for 10 to 30 minutes, the exact time depending on the temperature of the operation. This causes the parts of the gelatine which have not been affected by the light to swell and thus form, in relief, an image of the picture previously taken. The gelatine plate is laid flat, gelatine surface up, and across one end some of the liquid or moldable semi-liquid composition hereinafter described is poured. A backing sheet, of celluloid or other material, is then placed above the gelatine sheet and by means of a heavy roller the backing sheet is squeezed down upon the swollen gelatine plate and the bulk of the viscous liquid composition gradually pushed forward toward the other end of the gelatine plate and the excess of the liquid composition finally pushed out and discarded. The moldable composition is then allowed to harden and set to the final product. The time required for solidification of the composition depends upon the viscosity

and air conditions but averages approximately 10 minutes.

The backing sheet with the solidified material immutably adhering thereto constitutes the printing plate and the whole is now stripped from the gelatine relief plate and allowed to completely solidify by exposure to the air for several hours. It is then ready to be put on a roll and roto-gravure printing begun. Either half tone or intaglio printing plates may be made by following the above general procedure, using, of course, the proper type of screen, as recognized by those skilled in this art.

I have found that cellulose nitrate constitutes an excellent base material. A composition which runs approximately 25% of nitro-cellulose provides a finished printing material of great hardness and durability. In general the greater the percentage of cellulosic base (considering the solids exclusive of solvents) that can conveniently be used without destroying the necessary initial molding plasticity of the product, the greater will be the hardness and durability of the finished solidified product. I have found that a composition made from a cellulosic nitrate base of low viscosity does not make as hard a material as a composition made from a cellulosic base of relatively high viscosity, but the hardest material is made from a mixture of cellulosic bases of varying viscosities. In order to get a plastic which will flow at the desired rate for molding purposes when a particular solvent is used and to obtain a liquid composition containing total solids of 20% to 35% or more, it is preferable to use a mixture of cellulosic bases of varying viscosities. Such a mixture may comprise part $\frac{1}{2}$ second cellulose nitrate and part cellulose nitrate of a higher viscosity such as part 4 second cellulose nitrate and part 40 second cellulose nitrate. Cellulose acetate also constitutes a valuable cellulosic base material.

I have found that as a rule, plasticizers, and particularly plasticizers such as camphor, castor oil and the like, have a tendency to decrease the hardness of the finished product. It is necessary, however, to add some plasticizer to the ingredients used in order that the composition be sufficiently plastic for initial molding purposes. Preferred plasticizers for cellulose nitrate are tricresyl phosphate, triphenyl phosphate, or dibutyl phthalate, and for the cellulose acetate I find that triacetin is a satisfactory plasticizer. These plasticizers, when used in the small amounts needed, appear to have very little effect on the hardness of the finished material, and yet give the material the desired plasticity and toughness. To increase still further the hardness and life of the material, certain gums or resinoids, such as gum dammar, may be added. The gums chosen should be gums which are substantially

insoluble in the vehicle of the printing ink which is used. Such gums in the material, however, will somewhat delay the hardening and setting of the finished product.

5 As solvents for the cellulosic base, acetone, ethyl acetate, butyl acetate, amyl acetate, butyl alcohol and similar well-known solvents in commercial use may be used. To obtain the best results, the solvent which should be used will depend somewhat on the particular cellulose base which is used. If cellulose nitrate is used as the base material, I have found that ethyl acetate and butyl acetate are especially valuable. Very effective results, where cellulose nitrate is used, 10 can be obtained by using a mixture of two solvents, i. e., technical butyl acetate (this contains some butyl alcohol) and ethyl acetate. If a material possessing very rapid setting and hardening characteristics is desired, ethyl acetate also serves as an excellent solvent. However, if a material possessing great hardness, sharpness and durability is desired, as for example a material initially moldable to form a printing plate for fine detailed printing, I prefer to use a mixture of butyl acetate and butyl alcohol with a small amount of ethyl acetate added. Pure ethyl acetate is a less desirable solvent where a fine printing form is to be made since the fine imprints and details carried by the copy relief are 20 not so accurately and sharply copied by an initially plastic cellulosic composition having ethyl acetate as the sole solvent. Furthermore, ethyl acetate evaporates very quickly with corresponding rapid hardening of the plate. Where quick hardening is a major consideration, and where exact impressions are not of primary importance ethyl acetate provides an excellent solvent. Acetone and amyl acetate have proven to be particularly valuable solvents where cellulose acetate is used as base material.

40 All the materials should be as free from water as possible. Any appreciable amount of water in the ingredients used greatly decreases the solubility of the cellulosic base. The commercial products mentioned, are, however, normally free from water, so that no difficulty is encountered in obtaining materials capable of forming a composition of desired characteristics.

My preferred composition when in liquid form contains 12 to 35% of total solids and 65 to 80% of solvents. The solids comprise preferably cellulose nitrate, with a small amount of plasticizer added. I have found that a mixture of cellulose nitrate material of varying viscosities generally produces a harder, tougher and more desirable hardened product. The mixtures of cellulose nitrate should be so selected as to achieve this end. An excellent mixture comprises $\frac{1}{2}$ second cellulose nitrate approximately 50%, 4 second cellulose nitrate approximately 10%, and 40 second cellulose nitrate approximately 40%. Any of these amounts might be increased with corresponding reductions in the others. As plasticizers, I have found triphenyl phosphate or tricresyl phosphate or dibutyl phthalate to be among the best and should be used in small or moderate percentages, of from 1 to 5% of the total composition. As solvents, mixtures of commercial butyl acetate and ethyl acetate seem to be the best, but amyl acetate may also be used. Commercial butyl acetate generally carries about 20% butyl alcohol, which is not objectionable. A small amount of benzene or similar cheaper solvent may be used to reduce the cost.

75 The particular portions and ingredients which

I have found to be especially valuable may be described as follows:—

Example 1

A composition giving a printing plate of great hardness and durability and which will faithfully copy the finest surface impressions may be made from a mixture comprising 25% by weight of total solids and 75% by weight of solvents. The total solids comprise 20% triphenyl phosphate, 20% 40 second cellulose nitrate, and 60% $\frac{1}{2}$ second cellulose nitrate. The solvent used comprises a mixture of 58% amyl acetate and 42% butyl acetate. Giving the quantities by weight and in total percentages this composition comprises 15% $\frac{1}{2}$ second cellulose nitrate, 5% 40 second cellulose nitrate, 5% triphenyl phosphate, 43.5% amyl acetate and 31.5% butyl acetate. This composition has a viscosity of 12 seconds (by falling ball test).

Example 2

A composition comprising total solids 25% by weight and solvents 75% by weight. The total solids comprise 20% triphenyl phosphate, 40% 40 second cellulose nitrate, and 40% $\frac{1}{2}$ second cellulose nitrate. The solvents used are substantially the same as given in Example 1 containing about 58% amyl acetate and 42% butyl acetate. Giving the quantities by weight and in total percentages this composition comprises 10% $\frac{1}{2}$ second cellulose nitrate, 10% 40 second cellulose nitrate, 5% triphenyl phosphate, 43.5% amyl acetate and 31.5% butyl acetate. This composition has a viscosity of 70 seconds (by falling ball test).

Example 3

A composition comprising 25% by weight of solids and 75% by weight of solvents. The solids comprise 5% tricresyl phosphate, 71% $\frac{1}{2}$ second cellulose nitrate, and 24% 40 second cellulose nitrate. The solvent used is ethyl acetate unmixed with any other material. Giving the quantities by weight and in total percentages this composition comprises 17.75% $\frac{1}{2}$ second cellulose nitrate, 6% 40 second cellulose nitrate, 1.25% tricresyl phosphate and 75% ethyl acetate. This composition has a viscosity of 39 seconds (by falling ball test).

Example 4

A composition comprising 25% by weight of solids and 75% by weight of solvents. The total solids comprise a mixture of 5% tricresyl phosphate, 64% $\frac{1}{2}$ second cellulose nitrate, and 31% 40 second cellulose nitrate. The solids above described are dissolved in technical butyl acetate, which comprises 75% of the total mixture. Giving the quantities by weight and in total percentages this composition comprises then, 16% $\frac{1}{2}$ cellulose nitrate, 7.75% 40 second cellulose nitrate, 1.25% tricresyl phosphate and 75% technical butyl acetate. The composition as above named has a viscosity of 52 seconds (by falling ball test).

Example 5

A composition comprising total solids 35.6% by weight and solvents 64.4% by weight. The total solids comprise 5.2% triphenyl phosphate, 8.3% gum dammar, 43.25% $\frac{1}{2}$ second cellulose nitrate, and 43.25% 40 second cellulose nitrate. The solvents used comprise 66.1% butyl acetate, 27.8% ethyl acetate and 6.1% of gum dammar solvents. The solvents for the gum dammar comprise 42%

benzene, 9.2% ethyl acetate, 8.1% acetone and 40.7% methyl alcohol. Giving the quantities by weight and in total percentages this composition comprises 15.4% $\frac{1}{2}$ second cellulose nitrate, 15.4% 40 second cellulose nitrate, 1.9% triphenyl phosphate, 2.9% gum dammar, 42.6% butyl acetate (technical), 17.9% ethyl acetate, and 3.9% gum dammar solvent. This composition has a viscosity of 800 seconds (by falling ball test). It is noted that this material has a high viscosity and if, for certain purposes, it is found too viscous to mold properly, its viscosity can be lowered by adding butyl acetate or ethyl acetate.

Example 6

A composition comprising total solids of 27.4% by weight and solvents 72.6% by weight. The solids comprise 10.5% triphenyl phosphate, 17% gum dammar, and 72.5% 40 second cellulose nitrate. The solvents used comprise 64% technical butyl acetate, 26.2% ethyl acetate, 9.8% gum dammar solvent. The gum dammar solvents used may be the same as that given in Example 5. Giving the quantities by weight and in total percentages this composition comprises 19.9% 40 second cellulose nitrate, 2.8% triphenyl phosphate, 4.7% gum dammar, 46.5% technical butyl acetate, 19% ethyl acetate, and 7.1% gum dammar solvent. This composition has a viscosity of 105 seconds (by falling ball test).

Where the composition is composed of only cellulose nitrate, a plasticizer and a solvent, it does not matter in what order they are mixed. The resulting solution, however, requires some time and stirring before it reaches complete homogeneity. When completely dissolved and mixed, the material should be filtered and is then ready for use.

When a gum or resin such as gum dammar is used it is preferable to dissolve the gum in its own solvent and later add this solution to the material above described. The gum solvent which should be selected will depend upon the gum or resin chosen, but in general it will consist of an anhydrous mixture of benzene, methyl alcohol and possibly other solvents such as acetone and ethyl acetate. The gum solution is added to the cellulose base solution and the two are mixed by stirring together. The final material is filtered and is then ready for use.

The moldable composition which is to be applied to the gelatine copy relief, as noted above, is very viscous. It has been found that the preferred viscosity is such that the material, while moldable, is not of itself freely flowable (like a spraying or brushing lacquer) but requires a considerable degree of mechanical pressure to force it into the fine macroscopic depressions of the copy relief. On the one hand the material should be sufficiently flowable to be forced into such depressions and on the other hand must not be so fluid as to freely enter such depressions. In the latter case, as where the material has a high percentage of solvents, subsequent evaporation of the solvent causes shrinkage of the mass during the hardening process, resulting in poor work. The material employed in actual practice is of such viscosity that it is substantially self sustaining and a mass of the material placed on a swollen gelatine sheet would not, within any reasonable time, flow over the sheet. The viscosity characteristics are therefore of salient importance.

The finished material generally is semi-transparent and water colored. It may be found desirable in certain instances to give the material

a distinctive color. I have found, for example, that the material can be colored without harm thereto by adding a coloring material dissolved in a suitable solvent, for example, .01 g. of oil red, or oil orange, or other color, dissolved in 5 cc. of ethyl acetate.

My composition material gives a product which is only slightly thermoplastic and hardens first by absorption of the solvent by the backing sheet (if one is used), secondly by precipitation processes when the plastic composition material contacts with the moisture and water carried by the water swollen gelatine copy relief, and finally by evaporation of the residual solvent through exposure of the material to the air.

As many changes can be made in the steps and ingredients used without departing from the scope of my invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What I claim is:

1. A hardenable composition for forming printing plates comprising predetermined proportions of cellulosic materials of different viscosity, and a sufficient amount of an organic plasticizer to render the cellulosic materials non-brittle, the composition having a viscosity in excess of ten seconds.

2. An improved printing plate comprising a nitro-cellulose base and a plasticizer, the nitro-cellulose including a plurality of compositions of differential viscosity.

3. A moldable composition for printing plates, comprising a mixture of nitro-cellulose compositions, a plasticizer comprising an aryl phosphate, and sufficient volatile solvent to render the mass workable, but insufficient to render the mass free flowable, the viscosity characteristics of the composition being such that mechanical pressure is required to force the material into the cavities or depressions of the order of those obtaining in a differentially swollen sensitized gelatine sheet.

4. A hardenable composition for printing plates comprising a plurality of cellulosic materials of differential viscosity, and a relatively large quantity of a volatile anhydrous solvent, the composition having such a viscosity that mechanical pressure is required to force the composition into depressions of the order of those obtaining in a sensitized water swollen gelatine relief copy.

5. A hardenable composition for printing plates and the like, comprising cellulose ester materials of differential viscosity, a resinoid, a small quantity of a plasticizer, and a sufficient quantity of a volatile solvent to render the mass workable, the composition having a viscosity in excess of ten seconds.

6. A hardenable composition for printing plates comprising cellulose nitrate materials, a small amount of triphenyl phosphate, dissolved in a mixture of ethyl acetate and butyl acetate, the composition having a viscosity of between 10 and 100 seconds.

7. A potentially hardenable composition for printing surfaces comprising approximately 20% of a cellulose ester mixture, a minor percentage of a plasticizer, and approximately 75% of a volatile solvent, the viscosity of the composition being such that mechanical pressure is required to force it into depressions of the order of those obtaining in a sensitized water swollen gelatine sheet.

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