March 9, 1943. G. F. NADEAU ET AL 2,313,570

PHOTOGRAPHIC LAYER CAPABLE OF RECEIVING WRITING

Filed Sept. 25, 1940

FIG. 1

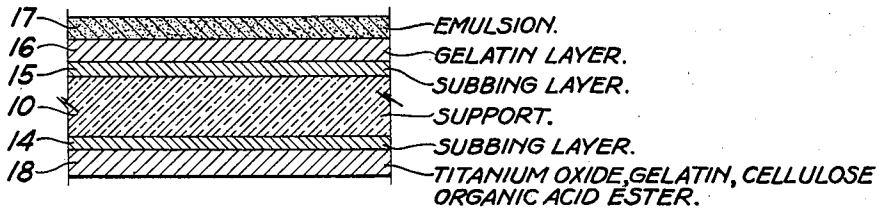


FIG. 2

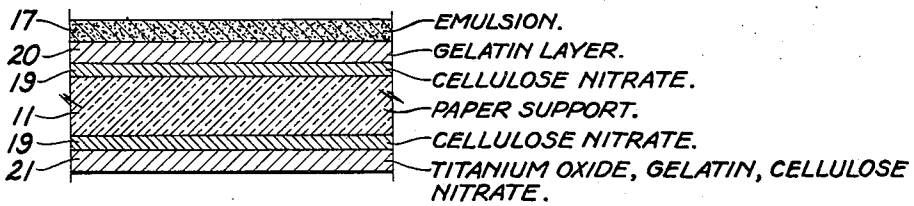


FIG. 3

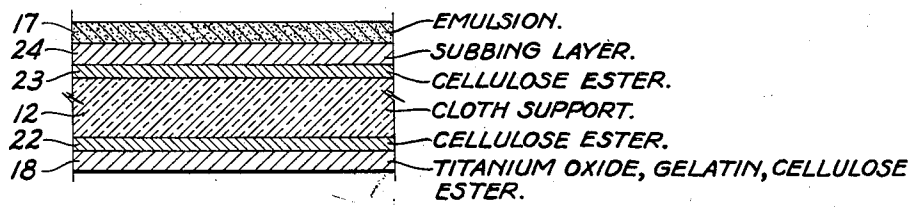
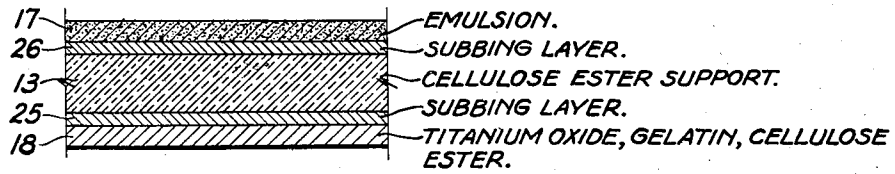


FIG. 4



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Patented Mar. 9, 1943

2,313,570

UNITED STATES PATENT OFFICE

2,313,570

PHOTOGRAPHIC LAYER CAPABLE OF RECEIVING WRITING

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Application September 25, 1940, Serial No. 358,274

13 Claims. (Cl. 95—8)

This invention relates to a sensitized photographic element and particularly to an element provided with a pigmented layer designed to receive writing.

It is a well known practice to waterproof paper, cloth and similar materials which are highly susceptible to moisture by the application of non-moisture absorbing layers to the surfaces of these materials. As applied to the various sensitized photographic products, it is the practice to employ in these layers cellulose esters, polymerized vinyl compounds and similar water resisting substances. A photographic paper such as a direct positive paper, which is designed to render a positive image in a minimum of time, requires a support which will not be substantially wetted by processing solutions and can be delivered in practically a dry condition, often within the space of a few minutes. Such a paper has been described in the prior U. S. Patent No. 1,933,824, granted November 7, 1933.

Frequently it is desired to write or print with ink onto the back of such a paper and this is generally prevented by the thoroughness with which the paper has been waterproofed. Likewise the surface of the paper may refuse to take pencil markings unless it is especially prepared to receive pencil records.

The same difficulties are encountered in the use of sensitized tracing cloths such as are described in the prior U. S. Patent 2,117,814 granted May 17, 1938. While the tracing cloth may be satisfactorily waterproofed so as to resist the softening effect of processing solutions it is generally impossible to imprint satisfactory pencil or ink records thereupon. Likewise photographic film which is now in general use will not readily take pencil or ink impressions. By its very nature the film is resistant to aqueous solutions such as ink and the smooth surfaces will not retain pencil marks.

The principal object of the present invention is to overcome these difficulties by providing sensitive photographic products with a pigmented layer which will take either ink or pencil.

This object is accomplished by depositing upon a water proof support a layer consisting of an inorganic pigment such as titanium oxide, baryta, chalk, or lithopone; a hydrophilic material such as gelatin and a cellulosic material such as cellulose organic and inorganic esters and cellulose ethers. We may also use resins in place of the cellulosic compounds, and, in the preferred embodiment of our invention, titanium oxide as the pigment.

In the accompanying drawing, Fig. 1 is a cross section illustrating the relation of the pigmented layer to the support and emulsion layer.

Fig. 2 is a cross section of a sensitive photographic paper provided with cellulose nitrate waterproofing layers, the pigmented layer, and an emulsion layer adhesively joined to the support.

Fig. 3 is a cross section illustrating the apppli-cation of the invention to a sensitized tracing cloth. The pigmented layer is disposed on one side of the waterproofed cloth support and the emulsion layer is adhesively joined to the other side.

Fig. 4 is a cross section illustrating the general arrangement of layers comprising a sensitive photographic film provided with a titanium oxide layer capable of receiving ink and pencil marks.

In the operation of our invention we apply the titanium oxide containing layer from solvent solutions of which the following is typical.

	Per cent
Cellulose nitrate	1.2
Gelatin	1.2
Acetic acid	2.0
Water	5.0
Acetone	50.0
Methanol	40.6

To this formula is added the titanium oxide. For our purposes a 2–5% concentration is sufficient. The pigmented sub is then coated upon a waterproof support and allowed to dry.

We will now describe our invention by particular reference to the accompanying drawing. In the general operation of the invention as shown in Fig. 1, the support 10 is coated on both sides with the subbing layers 14 and 15. These layers may consist of the same or different materials. For instance, 14 may be cellulose nitrate, cellulose acetate, or cellulose acetate-propionate but usually 15 consists of cellulose nitrate, ordinary gelatin being applied over this to serve as an adhesive layer 16 for the emulsion 17. Otherwise, if 15 is not cellulose nitrate, adhesive layers consisting of for instance gelatin and a synthetic resin or gelatin coated from a solution of water, acetic acid, acetone, and methanol are used to get the proper adhesion and flexibility. The titanium oxide containing layer 18 is applied directly over layer 14 and may contain in addition to the oxide, gelatin and any cellulose ester.

Fig. 2 illustrates the use of a paper support 11 coated with the cellulose nitrate on both sides, layers 19, although these may be other cel-

lulose esters or mixed esters; the adhesive layer **20** which may be gelatin joins the emulsion layer **17** to layer **19**. On the opposite side the mixed titanium oxide, gelatin, and cellulose nitrate layer **21** is coated over the nitrate layer **19**. The support may be a glossy paper which has previously been baryta sized and according to the invention is then waterproofed, emulsion coated on the glossy side, and pigment coated on the back.

Fig. 3 shows the cloth support **12** double coated with cellulose layers **22** and **23** which may consist of the same, different, or mixed cellulose esters. The adhesive subbing layer **24** joins the emulsion **17** to layer **23** and on the opposite side of the support the mixed titanium oxide, gelatin, and cellulose ester layer **18** is coated over layer **22**. Layers **22** and **18** may contain the same or different cellulose esters.

Fig. 4 illustrates the method of application of the titanium oxide containing layer **18** to a cellulose ester support **13** which may be opaque or transparent. In this case due to the water resitsant nature of the cellulose ester support it is not necessary to coat it with waterproofing layers; therefore subbing layers **25** and **26** comprising, for instance, gelatin are applied followed directly by the emulsion layer **17** on one side, and on the opposite side, the mixed titanium oxide, gelatin and cellulose ester layer. Should **18** contain a cellulose ester other than cellulose nitrate it may be desirable to incorporate into layer **25** a material such as a synthetic resin to aid in obtaining the proper flexibility and adhesion between layers **18** and **25**.

It will be noted that the general technique of our invention consists in applying an emulsion layer and a pigmented layer to a waterproof support. Should the pigmented layer comprise a cellulose ester which does not adhere well to the waterproof support it may be desirable to add to the subbing layers **14**, **22**, or **25** a material such as a resin. Should the emulsion layer not adhere well or give the proper flexibility when coated upon subbing layers such as 15 or 23 a material such as a synthetic resin is added to the adhesive layer. This technique is more fully described in U. S. Patents 2,096,616; 2,096,617; 2,096,675. In an alternative method we use a gelatin subbing solution containing a high percentage of acetone, for instance, 66% acetone, 5% water, 25% methanol, 2% gelatin and 2% acetic acid to sub a cellulose acetate layer which is to receive an emulsion.

The following example further illustrates the manner of carrying out our invention.

A glossy double-weight baryta-coated photographic paper was coated on both sides with a dope of cellulose nitrate of the following composition:

	Per cent
Cellulose nitrate	4
Amyl acetate	76.4
Methanol	9.5
Acetone	9.5
Triphenyl phosphate	0.6

This is followed by a thin coating of the following composition on the back side:

	Per cent
Cellulose nitrate	2
Amyl acetate	78.3
Methanol	9.7
Acetone	9.7
Triphenyl phosphate	0.3

On top of this second coat on the back side of the paper is applied a coating from a dope of the following composition:

	Per cent
Cellulose nitrate	1.2
Gelatin	1.2
Acetic acid	2.0
Water	5.0
Acetone	50.0
Methanol	40.6

to which 3% titanium oxide has been added. On the glossy side of the paper was coated a gelatin layer from a solution of which the following is typical.

	Per cent
Gelatin	1.2
Water	3.0
Acetic acid	2.0
Methanol	94.0

It is not always necessary to double coat a support with a cellulose ester but some supports having substantially long protruding fibers are best rendered completely waterproof and smooth by such a technique.

The cellulose nitrate which we use as a constituent of the pigmented layer or the subbing layers may be a highly alcohol soluble one containing 10–12%, preferably 11% of nitrogen. Instead of a single light sensitive emulsion layer we may employ a plurality of differentially light sensitive emulsion layers containing light filter or sensitizing dyes or color formers or other material which adapt the element to use in the taking or reproduction of color pictures in color. Here again we are not limited to any specific cellulose ester for use throughout the element.

Having thus described our invention, what we declare is new and desire to secure by Letters Patent of the United States is:

1. A sensitive photographic element designed to receive writing comprising, a support coated on both sides with a subbing layer of a material selected from the group consisting of gelatin and cellulose ester, a pigmented layer consisting of a mixture of an inorganic pigment, gelatin, and a cellulose compound over the subbing layer on one side of said support and on the opposite side a light sensitive emulsion layer adhesively joined to a subbing layer.

2. A sensitive photographic element designed to receive writing comprising, a support coated on both sides with a cellulose ester subbing layer, a pigmented layer consisting of a mixture of titanium oxide, gelatin, and a cellulose ester over the subbing layer on one side of said support, and on the opposite side a light sensitive emulsion layer adhesively joined to a subbing layer.

3. A sensitive photographic element designed to receive writing comprising, a support coated on both sides wth a cellulose ester subbing layer, a pigmented layer consisting of a mixture of titanium oxide, gelatin, and cellulose nitrate over the subbing layer on one side of said support, and on the opposite side a light sensitive emulsion layer adhesively joined to a subbing layer.

4. A sensitive photographic element designed to receive writing comprising, an opaque support coated on both sides with a cellulose nitrate waterproofing layer, a pigmented layer consisting of a mixture of titanium oxide, gelatin, and cellulose nitrate over the waterproofing layer on one side of said support, and on the opposite side a light sensitive emulsion layer adhesively joined to the waterproofing layer.

5. A sensitive photographic element designed to receive writing comprising, a paper support coated on both sides with a cellulose nitrate waterproofing layer, a pigmented layer consisting of a mixture of titanium oxide, gelatin, and cellulose nitrate over the waterproofing layer on one side of said support, and on the opposite side a light sensitive emulsion layer adhesively joined to the waterproofing layer.

6. A sensitive photographic element designed to receive writing comprising, a cloth support coated on both sides with a cellulose nitrate waterproofing layer, a pigmented layer consisting of a mixture of titanium oxide, gelatin, and cellulose nitrate over the waterproofing layer on one side of said support, and on the opposite side a light sensitive emulsion layer adhesively joined to the waterproofing layer.

7. A sensitive photographic element designed to receive writing comprising, a paper support coated on both sides with a cellulose acetate waterproofing layer, a pigmented layer consisting of a mixture of titanium oxide, gelatin, and cellulose nitrate over the waterproofing layer on one side of said support, and on the opposite side a light sensitive emulsion layer adhesively joined to the waterproofing layer.

8. A sensitive photographic element designed to receive writing comprising, a paper support coated on both sides with a cellulose acetate-propionate waterproofing layer, a pigmented layer consisting of a mixture of titanium oxide, gelatin, and cellulose nitrate over the waterproofing layer on one side of said support, and on the opposite side a light sensitive emulsion layer adhesively joined to the waterproofing layer.

9. A sensitive photographic element designed to receive writing comprising, a paper support coated on both sides with a cellulose acetate waterproofing layer, a pigmented layer consisting of a mixture of titanium oxide, gelatin, and cellulose acetate over the waterproofing layer on one side of said support, and on the opposite side a light sensitive emulsion layer adhesively joined to the waterproofing layer.

10. A sensitive photographic element designed to receive writing comprising, a cloth support coated on both sides with a cellulose acetate waterproofing layer, a pigmented layer consisting of a mixture of titanium oxide, gelatin, and cellulose nitrate over the waterproofing layer on one side of said support, and on the opposite side a light sensitive emulsion layer adhesively joined to the waterproofing layer.

11. A sensitive photographic element designed to receive writing comprising, a cloth support coated on both sides with a cellulose acetate-propionate waterproofing layer, a pigmented layer consisting of a mixture of titanium oxide, gelatin, and cellulose nitrate over the waterproofing layer on one side of said support, and on the opposite side a light sensitive emulsion layer adhesively joined to the waterproofing layer.

12. A sensitive photographic element designed to receive writing comprising, a cloth support coated on both sides with a cellulose acetate waterproofing layer, a pigmented layer consisting of a mixture of titanium oxide, gelatin, and cellulose acetate-propionate over the waterproofing layer on one side of said support, and on the opposite side a light sensitive emulsion layer adhesively joined to the waterproofing layer.

13. A sensitive photographic element designed to receive writing comprising, a cellulose acetate support coated on both sides with a cellulose nitrate subbing layer, a pigmented layer consisting of a mixture of titanium oxide, gelatin, and cellulose nitrate over the subbing layer on one side of said support, and on the opposite side a light sensitive emulsion layer.

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