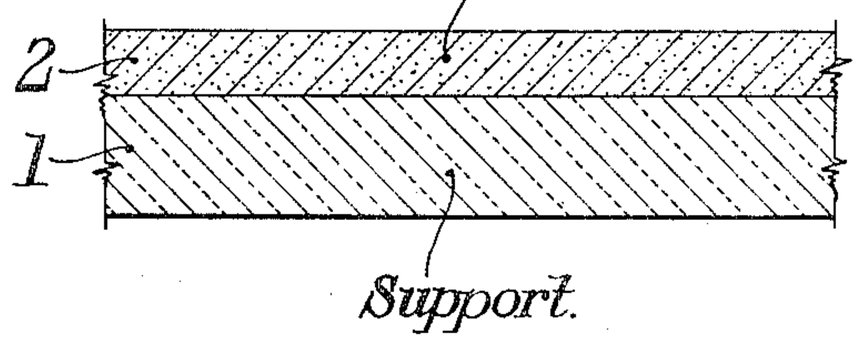
Jan. 23, 1934. M. MARTINEZ 1,944,293

PHOTOGRAPHICALLY SENSITIVE ELEMENT

Original Filed Nov. 17, 1930

Sensitive coating capable after exposure of development into a relief image by heat alone.



Inventor:
Michele Martinez,

By Newton M. Perrin

Attorney.

Patented Jan. 23, 1934 1,944,293

UNITED STATES PATENT OFFICE

1,944,293

PHOTOGRAPHICALLY SENSITIVE ELEMENT

Michele Martinez, London, England

Original application November 17, 1930, Serial No. 496,341. Divided and this application March 26, 1932. Serial No. 604,316

5 Claims. (Cl. 95—7)

This application is a division of my application, Serial No. 496,341, filed November 17, 1930, and relates to a new sensitive material useful in producing images in relief for photographic, photomechanical and other purposes. This new material, after being activated, is developable by heat alone into a relief image.

I have found useful compositions containing a metal ion and the ions of organic acids of the type which permit reduction of the metal upon treatment with light or other effective reagent. Such a composition in a suitable carrier such as gelatin or other colloid, may be coated in a layer, dried, exposed to an image and heated with the result that the colloid layer swells, producing a marked relief at the exposed points.

Among the salts found by me to be most suitable for the introduction of the ions above defined are following: ferric salts such as ferric ammonium citrate, ferric ammonium oxalate, ferric chloride, ferric sulphate, mercuric chloride and mercuric sulphate, and other salts of heavy metals; or light sensitive compounds of a heavy metal such as cobaltimine.

As an acid constituent, I find useful any carboxylic acid soluble in the mixture, and particularly oxalic, citric, tartaric or lactic acid. To these, acid salts may be added, such as sodium acid phosphate.

I will now describe various embodiments of my invention, but it is to be understood that, while certain of these are preferred, they are all mentioned as examples capable of wide variation.

Reference is made to the accompanying drawing, the single figure of which illustrates on a magnified scale a section of a photographic element embodying my invention.

The element consists of a support 1, preferably of paper, but it may be of any usual material upon which is coated a layer 2 of my improved sensitized coating, which may be made by any of the various methods described hereinafter.

The following formula constitutes one example of my invention.

EXAMPLE 1

Water	100 cc
Gelatin	40 grams
Ferric ammonium citrate	5 grams
Oxalic acid	3 grams

This mixture may be coated either by hand or machine on any suitable or usual support, such as film support, paper, glass, linoleum or metal. The coating is then dried. It is desirable that the drying should be relatively fast, as this will produce a coating which is faster to light for the cases where the coating is light printed.

Having now prepared the surface which is to furnish the relief, I may proceed in one of two ways.

The more common method, satisfactory in most cases, is next to expose the gelatin surface to a light image. This may be done by exposing to an image, as by contact printing under a positive or negative. The length of exposure required with a coated layer made similar to Example 1 will be of the order of three minutes to sunlight or an arc lamp. After completing the exposure the surface is exposed to moderate heat, as for example, before or over an electric heater or electric hot plate or in an oven, all of the type common in household use. Another method of applying heat and bringing out the relief is to pour over it a hot substance such as molten wax or metal of low melting point or by dipping in hot oil. The heating must be vigorous enough to bring up the required relief, but overheating must, of course, be avoided. The optimum temperature range I have found to be between 90 and 130° C., but do not limit myself to this range.

The second method is to prepare the image in the layer by chemical means and then heat as before. To accomplish this I may take any photo mechanical printing surface, or another relief image, moisten the surface of this with a substance which will reduce the metal salt in my coating, press into contact the surface thus moistened and the coated support, allow them to remain in contact for a short time, separate them, dry the coating, and then develop the relief by heating as before. Substances suitable for use as a reducer with coatings containing ferric salts are for example, solutions of stannous salts, such as stannous chloride, and sulphites, such as sodium sulphite. With coatings containing mercuric salts, solutions of stannous salts of sulphites may be used as a reducer, or a solution of ferrous sulphate containing potassium hydroxide. It will be best to leave the coating and the moistened image in contact for some time to insure a sufficiently complete conversion of the metal salts of the coating. After separating them, the coating is allowed to dry for a short time and is then heated to bring out the relief.

Another suitable formula for a coating is the following:

EXAMPLE 2

Water	100 cc.
Gelatin	40 grams
Ferric ammonium oxalate	10 grams

Another embodiment of my invention in which I have introduced certain improvements is shown in

EXAMPLE 3

Solution A

Water	100 c.c
Gelatin	40 grams
Ferric ammonium oxalate	8 to 12 grams
Ferric ammonium citrate	2 to 3 grams
Sodium oxalate	1.5 grams
Ammonium oxalate	1 gram
Oxalic acid	1.5 to 5 grams
Sodium acid phosphate	1 gram

This is dissolved by heat. To this is then added

Solution B

Water	100 cc.
Mercuric chloride	9 to 10 grams
Ammonium chloride	0.25 to 1 gram

In this formula it is not necessary to add solution B as indicated but in my opinion a slightly better coating and relief for some purposes can be obtained with its use. One to 3 grams of borax may be added to solution A to increase the hardness of the relief. If a precipitate forms when solution B is poured into solution A, a few drops of hydrochloric or nitric acid may be added. In this formula more oxalic acid gives a higher but coarser relief. The same is true of the sodium and the ammonium oxalates. The sodium phosphate may be omitted, but in my opinion it adds slightly to the quality of the coating.

Coating is done at any temperature above the melting point of the solution. As previously stated drying should be carried out in a darkened room and be moderately rapid, especially if the paper is to be light printed. It should be thoroughly dry when used.

The amount of relief depends upon the amount of gelatin coated on the support. With a very thick coating, a high relief can be obtained. A convenient method for securing a thick coating is to coat the support several times.

The thickness of the coating to obtain a relief most useful for the processes contemplated is preferably from .0005 to .0015 inch.

If too small a proportion of gelatin is used, for instance, less than half the quantities mentioned, the phenomenon does not occur to an extent useful for most purposes. That is, the amount of gelatine is preferably as great as or more than the sum of the other constituents, exclusive of water. The water, of course, largely evaporates after coating. The gelatine content of the dried coated layer is, therefore, about 50% or greater, and such a layer has qualities and properties that are lacking entirely in a layer not so constituted.

After exposure, the relief should preferably be developed within a few hourse, although little or no deterioration will be noted within two or three days.

After the relief is made, it is permanent though the surface may alter in color, particularly if mercury is used. It is understood, of course, that it must not be reheated as otherwise light exposed portions would tend to swell. The reliefs, when completed, should be kept in a fairly dry place.

The relief thus obtained is useful in various processes, particularly those pointed out in the parent application.

There is apparently unlimited range of materials that may be used as auxiliary to modify the results obtained and having various advantages and properties. For instance, lactic acid renders the layer, both before and after use, more flexible, and permits a higher swelling, apparently because of the softening action in the gelatine. The effect of sodium acid phosphate is to sharpen detail without affecting the height of the relief, and also to give a smoother and tougher surface. The surface of the relief is smooth and somewhat glossy.

Although the reactions and the mechanics involved in my invention are imperfectly understood, research indicates and it is my belief that, under the influence of heat, carbon dioxide is given off by one or more of the ingredients at the exposed points, and causes a cellular structure in the mass.

I have found that it is particularly desirable that there be a high ratio of carboxylic content, calculated as carbon monoxide, to ferric iron content. In Example 1, this ratio is 5.4; in Example 2, it is 3.0 and in Example 3 it is 2.5 to 5.6. In general I consider the lower limit of this ratio to be about .5 and it preferably should be well above 1.5 as indicated in the examples.

I consider as included within my invention all modifications and equivalents coming within the scope of the appended claims.

What I claim as new and desire to be secured by Letters Patent is:

1. A sensitive element including a support and a layer thereon capable by heat development of having relief images formed therein and comprising a colloid and substances yielding in aqueous solution carboxyl and ferric ions, the ratio of the carboxyl contents, calculated as carbon monoxide, to the ferric content being greater than 1.5.

2. A sensitive layer capable of having relief images formed therein by heat development and comprising gelatine, an organic acid yielding in aqueous solutions carboxyl ions and a ferric salt yielding in aqueous solutions ferric ions, the ratio of the carboxyl, calculated as carbon monoxide, to the ferric content being greater than 1.5.

3. A sensitive layer capable of having relief images formed therein by heat development and comprising gelatine, an organic acid yielding in aqueous solutions carboxyl ions and a ferric salt yielding in aqueous solutions ferric ions, the ratio of the carboxyl, calculated as carbon monoxide, to the ferric content being greater than 1.5, the layer having the property that upon exposure to light there is formed therein a substance which will react under the influence of heat to yield a gas, and the thickness of the layer being sufficient to entrap such gas.

4. A sensitive layer capable of having relief images formed therein by heat development and comprising gelatine, an organic acid yielding in aqueous solutions carboxyl ions and a ferric salt yielding in aqueous solutions ferric ions and having a thickness of at least .0005 inch the amount of gelatine in the layer being as great as the sum of the other constituents.

5. A sensitive layer capable of having relief images formed therein by heat development and comprising gelatine, an organic acid yielding in aqueous solutions carboxyl ions and a ferric salt yielding in aqueous solutions ferric ions, the ratio of the carboxyl, calculated as carbon monoxide, to the ferric content being greater than 1.5, and having a thickness of at least .0005 inch the amount of gelatine in the layer being as great as the sum of the other constituents.

MICHELE MARTINEZ.