April 10, 1934. M. MARTINEZ 1,954,325

PHOTOGRAPHICALLY PRODUCED GELATIN RELIEF

Original Filed Nov. 17, 1930

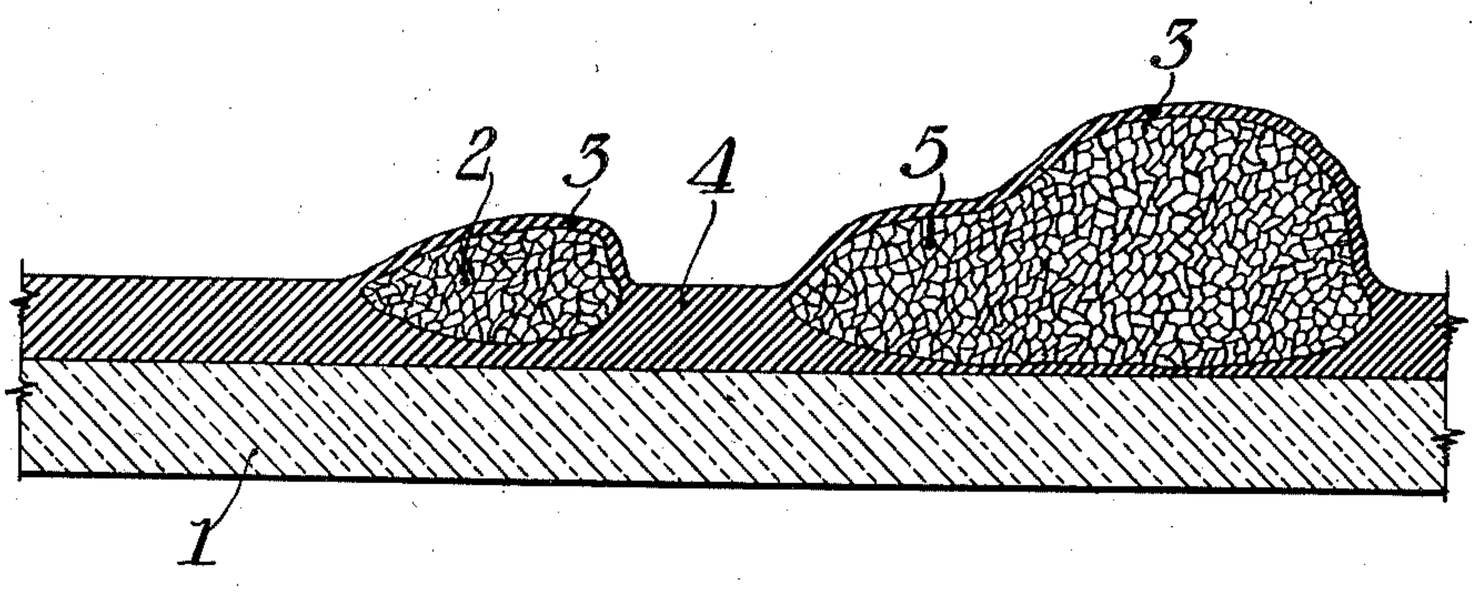

Fig. 1.

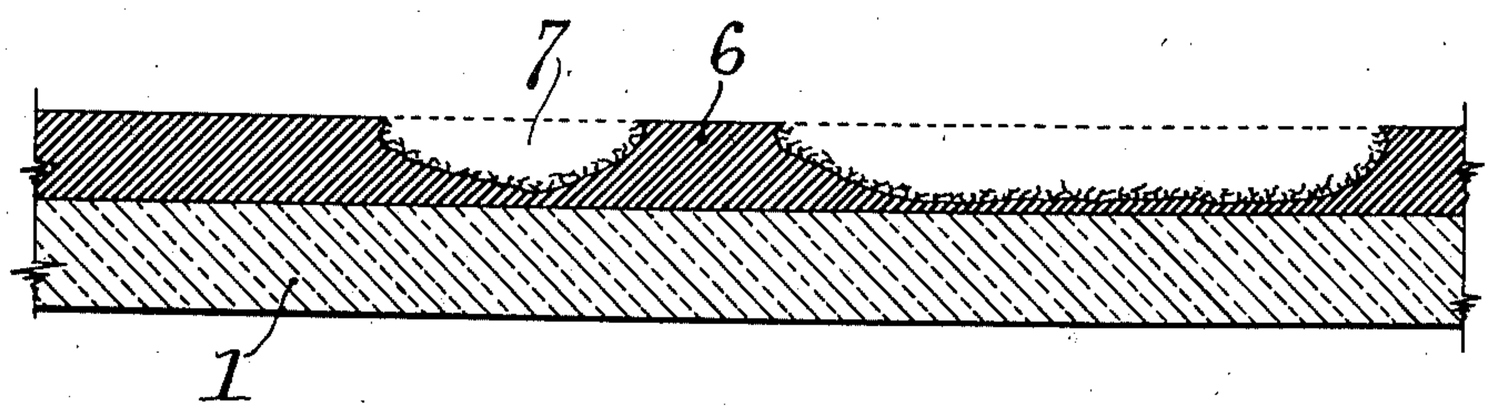

Fig. 2.

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PHOTOGRAPHICALLY PRODUCED GELATIN RELIEF

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Original application November 17, 1930, Serial No. 496,341. Divided and this application March 26, 1932, Serial No. 601,446

6 Claims. (Cl. 95—5.6)

This application is a division of my application, Serial No. 496,341, filed November 17, 1930 and relates to the product in the form of a relief obtained by the process described in that application. For the sake of completeness, the description of the material and of the process will be fully stated in this specification. For the sensitive material, 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 formulæ and procedures but it is to be understood that, while certain of these are preferred, they are all mentioned as examples capable of wide variation.

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. As indicated in the examples, the heating must be vigorous, that is, rather sudden, in order to bring up the required relief, but overheating must, of course, be avoided. A temperature range which I have found advantageous is between 90 and 130° C. but do not limit myself to this range. For instance, I have heated at a temperature of 200° to 210° for a short time, of the order of 10 seconds, with the result that a high relief was quickly developed; but such high temperatures should not be maintained for a materially longer period or the relief may be charred or blistered. If heated slowly, the relief is not so great; and if heated very slowly, no useful relief may be obtained due probably to the escape of the evolved gas without swelling the gelatin mass. In this case, much of this gas probably escapes through the support if of paper.

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 photomechanical 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 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, 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 in which I have introduced certain improvements is shown in

Example 3

Solution A.

Water	100 cc.
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 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 between .0005 and .0015 inches.

After exposure, the relief should preferably be developed within a few hours, 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 gelatin. 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 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 preferably it should be well above 1.5, as indicated in the examples.

The gelatin layer of the original material has the physical characteristics as to solubility, denseness and the like that are customary in any photographic gelatin layer containing non-hardening salts. When subjected to heat up to 200° C. there is no important change in the physical or photosensitive characteristics of the layer if the latter had not been exposed to light.

Where the layer has been exposed to a strong illumination, however, it yields, upon heating, at exposed points throughout its mass a gas (carbon dioxide) which, being expanded in situ by the heat, transforms the mass of the layer into a cellular or foamlike structure. If the layer is very thin the gas escapes without causing this expansion and it is necessary, therefore, that the layer be relatively thick in order to obtain a maximum relief effect.

Similarly gas forming at or near the surface of the layer escapes without expanding the surface portion and there is left thin skin which helps to seal this gas in the deeper part of the layer as it expands to produce the relief effect.

It will be seen that the resultant relief varies in thickness of the foamlike or cellular portion dependent on the original excitation and that the entire relief is covered by a thin, relatively hard skin which is smooth, tough and somewhat glossy. It is not so wear resistant, however, as to withstand repeated use as a printing member and accordingly a cast is made from it for such use.

Reference will now be made to the accompanying drawing, Figure 1 of which shows on an exaggerated scale a diagram of the new relief formed by my process, and

Figure 2 shows in a similar manner a relief obtainable from the form shown in Fig. 1.

In that figure, 1 indicates a support preferably of paper. This carries the gelatin relief which consists of two portions, an inner cellular relief of varying thickness as indicated at 2 and 5 and a tough skin 3 covering the entire relief. Where there has been no exposure as at the points marked 4, the entire layer is hard.

The principal uses of the process and product are in the photomechanical arts where the image is discontinuous and where there are dots or other figures composing the exposed or unexposed portions.

It will be apparent that the area of each dot and also the depth at which it is situated in the layer will be determined by the exposure.

It is possible, particularly if the relief is heated successively and the foam structure thus rendered very brittle, to scrape or rub away the cellular structure, leaving a relief as shown in Fig. 2, in which the unexposed portions 6 have the thick-

ness of the original coating and the exposed areas have become depressions 7. This relief image is capable of various uses but is not claimed herein being shown as part of the complete description of the physical properties of the relief image.

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

Having thus described my invention, what I claim as new and desire to secure by Letters Patent is:

1. An element including a colloid relief layer made by a photographic process including development by heat and comprising a support, a layer of varying thickness and of cellular structure and a dense, relatively tough skin covering the entire relief layer, the thickness of the relief layer being a function of the original exposure.

2. A colloid relief image formed by heat development and comprising a colloid layer with a thin relatively tough crust and a cellular relief image of variable thickness beneath said crust.

3. A gelatin relief image formed by heat development and comprising a layer with a thin, relatively tough crust and a cellular relief image of variable thickness beneath said crust.

4. A photographic element comprising a support and a layer thereon including a photographically formed relief image formed therein from a layer of uniform thickness, said image comprising solid, unexposed, unaffected areas of the original thickness of the layer and exposed areas of cellular structure expanded to a thickness greater than the original thickness of the layer.

5. A photographic element comprising a support and a gelatin layer thereon including a photographically formed relief image formed therein from a layer of uniform thickness, said image comprising unaffected, unexposed areas of solid gelatin having the thickness and density of the original layer and exposed areas of cellular structure having a thickness greater than the original thickness of the layer.

6. A photographic element comprising a support and a layer thereon including a photographically produced colloid relief image formed by exposure and heat development, said image comprising solid, unexposed, unaffected areas of minimum thickness and exposed areas of cellular structure of greater thickness and covered with a thin relatively tough crust.

MICHELE MARTINEZ.