Jan. 28, 1941. G. P. HAM 2,229,891

PHOTOGRAPHIC REDUCER

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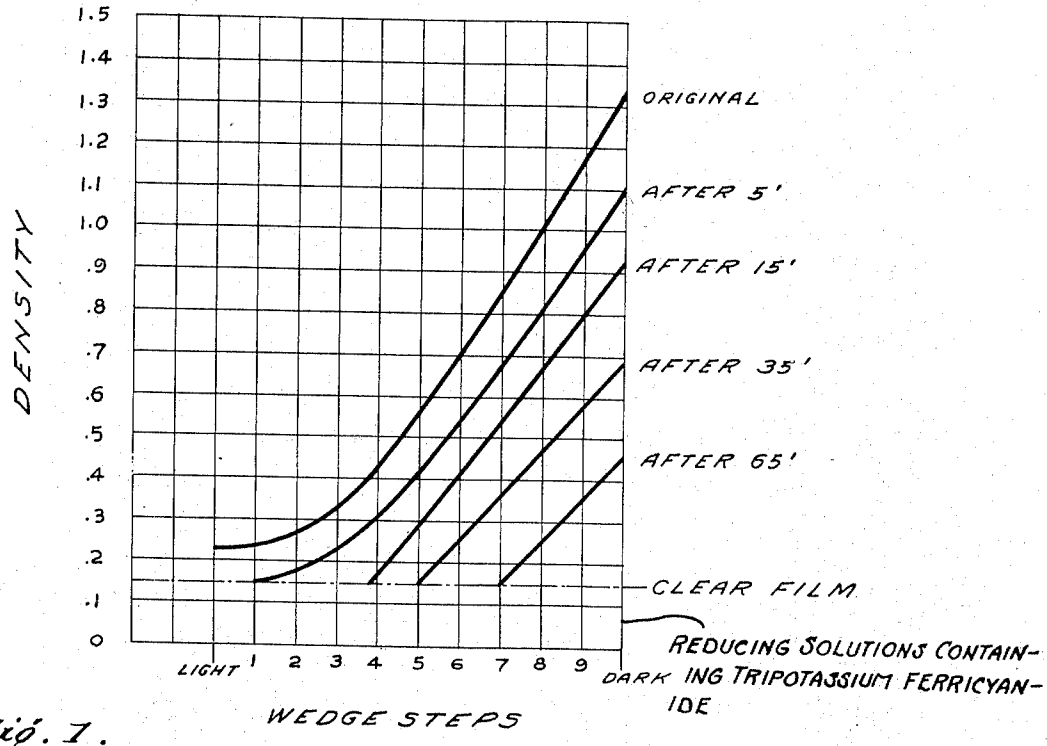


Fig. 1.

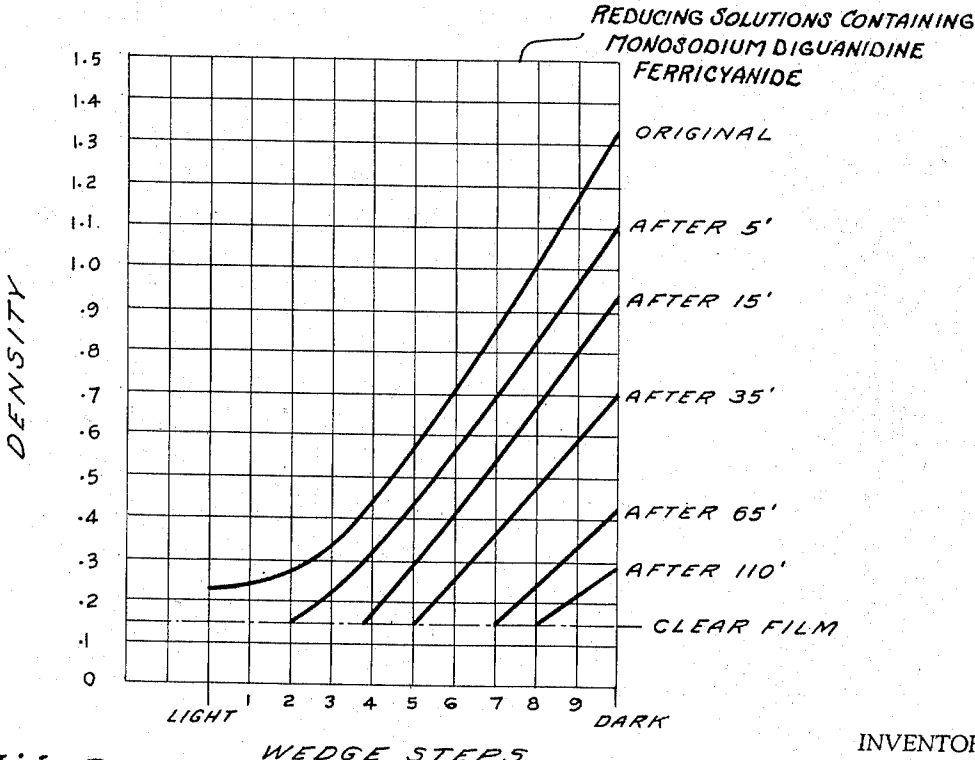


Fig. 2.

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PHOTOGRAPHIC REDUCER

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2 Claims. (Cl. 95—88)

This invention relates to new and improved reducing compositions for photographic material.

A number of reducing compositions have been developed to reduce the density of photographic material. These reducing compositions are of various types but in general may be classified into three main categories. First, cutting reducers, that is to say, reducers which take nearly or as much silver off the portions of the photographic material which have small amounts of silver corresponding to shadows in a negative or high lights in a positive, and hence result in an increase in contrast because the denser portions are not decreased proportionately as much. Typical of these reducing compositions are those employing ferricyanides. The second type is the so-called proportional reducers such as those using persulfates in which dense and light deposits are reduced proportionally and no change in contrast is effected. Finally, the third category is the super-proportional reducers in which the denser portions are reduced more than in proportion to the lighter deposits.

The present invention deals with compositions of the first category, that is to say, cutting reducers. In the past potassium ferricyanide has been used as the reducer, being referred to frequently as "Farmers solution," and a typical reducer of this type is represented by Eastman's R-4A.

The efficiency of a cutting reducer depends on two factors, one is the speed with which a given degree of reduction is effected, and the other, and more important, is the amount of contrast which is obtained, or putting it another way, the degree to which cutting is effected. It is particularly important to be able to cut correctly without too great a change in contrast. This is particularly important when it is desired only to cut the very lightest deposits, as for example, when an over-exposed or over-developed negative shows a fog. It is desired to cut out the fog without affecting the fidelity of the remaining image, and this should be effected as fast as possible because ferricyanide reducers have a softening action on the photographic emulsion and should be in contact for as short a period of time as is consistent with satisfactory cutting or reduction. Tripotassium ferricyanide has been the standard reagent in the "Farmers reducing solution" and it was believed that the action was due entirely to the ferricyanide and the cation was of no importance.

The present invention is based upon the discovery that the cation is not without significance and particularly that important results can be obtained when a sodium diamidine ferricyanide is used in place of the tripotassium ferricyanide, such as for example, monosodium diguanidine ferricyanide. The present invention produces a reducing composition which can be handled in exactly the same way as the standard potassium ferricyanide reducers but possesses advantages in that the cutting of the very lightest silver deposits takes place with extreme rapidity and the resulting image still retains good fidelity. In fact, the fidelity is actually improved to a greater degree than is possible with a similar degree of cutting with a potassium ferricyanide solution.

The present invention is not directed to any difference in procedure except the difference in the ferricyanide used and this is an advantage because the photographic technician is not required to modify his standard technique or procedure.

The results obtainable by the present invention are illustrated in the drawing in which:

Fig. 1 is a series of curves obtained by a reducing solution containing tripotassium ferricyanide; and

Fig. 2 is a similar set of curves obtained by a solution using a corresponding quantity of monosodium diguanidine ferricyanide.

The invention will be described in detail in the following specific example, it being understood that the invention is not limited to the exact proportions therein set forth, but is applicable to any other formula of ferricyanide reducer.

A photographic wedge with logarithmic steps representing a 50% increase in exposure from step to step, was contact printed onto a series of portions of 35 mm. super sensitive panchromatic film, using an extremely accurately controlled uniform exposure obtained by using as an exposing light a beam from a Leitz enlarger with the lens stopped down to its smallest opening. The series of strips of film were then developed in a single solution of Eastman DK 50 developer using stagnant development for 10 minutes at 18° C. They were then fixed with a standard Eastman F-5 fixer without using any special gelatin hardening solution other than the alum in the fixer. One of the strips was measured on a densitometer and the other strips were put in a reducer solution prepared as follows:

A solution of 8.60 grams of sodium diguanidine ferricyanide and 100 cc. of water was prepared, together with a second solution of 60 grams of sodium thiosulfate crystals and 250 cc. of water. 30 cc. of the first mixture and 120 cc. of the sec-

ond, were mixed and 850 cc. of water added. The strips were then passed in this mixture and the temperature maintained below 24° C. At the end of five minutes, one of the strips was removed and washed, at the end of 15 minutes, a second strip was removed and washed, followed by the third after 45 minutes, the fourth after 60 minutes, the fifth after 110 minutes. The reduced strips after drying were all read on the same densitometer and the densitometric curves are shown in Fig. 2 of the drawing.

A similar procedure was followed with a further number of strips by using 7.5 grams of tripotassium ferricyanide instead of 8.6 grams of sodium diguanidine ferricyanide. In this case no strip was measured at 110 minutes as the strip at that time showed departure from fidelity. All of the strips were read on the densitometer as before, and the densitometric curves appear on Fig. 1 of the drawing.

It will be noted that in both cases a sharp cutting was noted even after five minutes. The degree of cutting in the denser parts was practically the same but in the lighter deposits, whereas only the first wedge strip in Fig. 1 had been reduced to the minimum density determined by the inherent color of the clear gelatin, the second wedge strip had disappeared in Fig. 2. That is to say, while the potassium ferricyanide had only cut one wedge step the sodium diguanidine ferricyanide had cut two. At fifteen minutes and after, the behavior of reduction was substantially the same except that reduction could be continued for a longer time with the sodium diguanidine ferricyanide without losing fidelity. The rapid cutting of the smallest silver deposits with short exposure to the reducer which is noticeable with sodium diguanidine ferricyanide represents an important advantage because even with a very short treatment which will not seriously injure the gelatin, it is possible to cut fog and other veiling deposits which is the primary function of a cutting reducer. At the same time this is obtained without loss of fidelity, nor is there any staining of the gelatin.

What I claim is:

1. A method of reducing developed silver halide photographic material which comprises subjecting the material to a cutting reducer containing effective amounts of a sodium quanidine ferricyanide, the solution containing guanidine ions substantially corresponding to two-thirds of the stoichiometrical equivalent of the ferricyanide.

2. A cutting reducing solution for developed silver halide photographic material containing sodium guanidine ferricyanide and thiosulfate ions the guanidine ions substantially corresponding to two-thirds of the stoichiometrical of the ferricyanide.

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