Nov. 10, 1959 R. B. COLLINS ET AL 2,912,343

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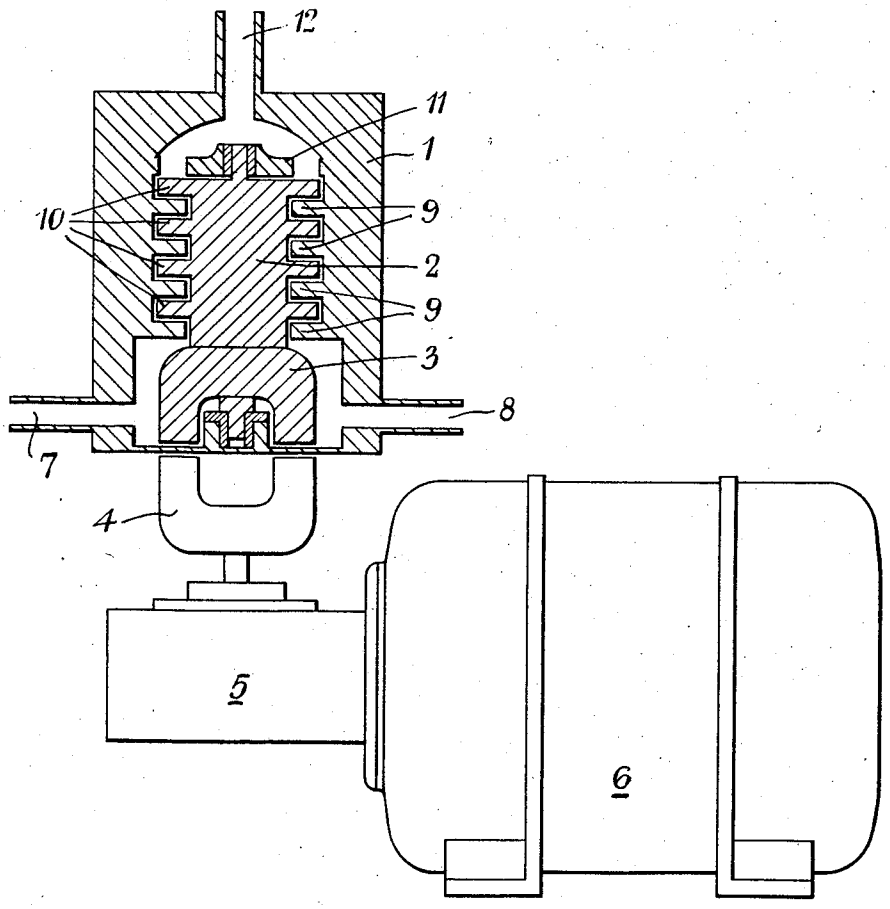
Filed Nov. 10, 1958



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United States Patent Office 2,912,343 Patented Nov. 10, 1959

2,912,343

PRODUCTION OF PHOTOGRAPHIC MATERIAL

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Application November 10, 1958, Serial No. 772,956

Claims priority, application Great Britain November 18, 1957

2 Claims. (Cl. 117—34)

This invention relates to the production of colour photographic materials.

In one main method of colour photography there is provided a photographic element which comprises a support carrying three silver halide photographic emulsion layers which are differentially sensitive to three regions of the visible spectrum, normally blue, green and red, and which contain compounds, so-called colour couplers, which will combine with the oxidation products of aromatic primary amino developing agents used to develop silver images in the layers to form dye images which are complementary to the utilised sensitivity of the respective layers.

Thus, for example, the photographic element may comprise the following layers in super position:

(*a*) Colourless film support.

(*b*) Silver halide emulsion layer sensitised to red light by means of an appropriate sensitising dye and containing a colour coupler yielding a cyan image.

(*c*) Silver halide emulsion layer sensitised to green light by means of an appropriate sensitising dye and containing a colour coupler yielding a magenta image.

(*d*) A yellow filter layer the colour of which may be readily destroyed.

(*e*) Silver halide emulsion layer having its natural sensitivity to blue light and containing a colour coupler yielding a yellow image.

The assembly may contain other layers, e.g. outer layers, masking layers, substratum and supercoat layers, according to the specific requirements in the product. The specified yellow filter layer (*d*) acts as a barrier to blue light reaching layers (*b*) and (*c*).

When such a layer is processed by exposure, development in an ordinary "black and white" developer, re-exposed, re-developed in a developer which is an aromatic primary amine such as N.N-diethyl-p-phenylene diamine, or its closely analogous compounds, and the silver removed from the product, there is obtained a film product which has positive images in cyan, magenta and yellow in layers (*b*), (*c*) and (*e*) respectively, and which thus presents by transmitted light a more or less true colour record of the subject to which the film was exposed.

Such colour photographic material is of relatively slow speed, and though several factors contribute to this, one important factor is that there is a tendency for the colour couplers which are added to the emulsion layers to reduce very considerably the photographic speed of the layers. This is particularly so in the case of the red-sensitised layer where the colour couplers yielding cyan dyes which are commonly used are phenolic compounds or naphtholic compounds. It appears probable that the colour coupler tends to displace the red-sensitising dye from the silver halide grains and thus, by reducing the effect of the dye, reduces the speed of the emulsion to red light very considerably. Attempts have been made to overcome this difficulty by a careful selection of red-sensitising dye (compare, for example, British Patent No. 625,992), but there are limits to this possibility and in fact no red-sesitising dye of adequate sensitising effect has yet been found which will be wholly unaffected by the addition to the emulsion of a phenolic type colour coupler.

It has now been found, however, that the reduction in speed of the emulsion consequent on the addition of the colour coupler takes place primarily while the emulsion is in liquid bulk form and will occur very much more slowly, if at all, after the emulsion has been coated and set as a layer on the support. Thus the emulsion, containing the colour coupler, deteriorates in speed with time so that, as it is coated, the speed of the coating obtained decreases with consequent change in colour balance.

According to the present invention, therefore, in the method of producing colour photographic materials which comprises applying to a support layer a silver halide photographic emulsion which contains a colour-sensitising dye and a colour coupler, or other compound the presence of which tends to reduce the sensitivity of the emulsion, the emulsion containing the colour-sensitising dye and a solution of the colour coupler or said other compound are intimately admixed in the required proportion at or near the site of the coating device and the mixture is coated with the minimum possible time delay between the time of mixing and the time when the emulsion is coated, and the coated emulsion is set and dried with the minimum of delay.

Various mechanical mixing devices known per se may be employed to produce the final emulsion for coating. Thus the emulsion and additive solution may be pumped as separate streams to a mixing cylinder and pass, via baffles, directly to the coating head of the coating machine.

Any of the well known methods of coating photographic emulsions may be employed, but generally one difference in working must be employed. In some methods part of the emulsion passing the coating head runs back to the coating head, i.e. the excess over the requirement (set by the thickness of the layer to be coated) is returned to the main bulk of emulsion. These methods cannot generally be employed in accordance with the present invention since it means that part of the emulsion leaving the coating head, and which is still deteriorating in speed owing to the effect of the additive, becomes mixed in with the fresh emulsion thus reducing its overall speed. Accordingly, such methods must generally be adopted with the variation that any run-back of emulsion is diverted and discarded. However, if the percentage run-back is not too excessive and the coating speed is fairly high, it is possible to set up equilibrium conditions in which, although there is some run-back, the photographic speed of the emulsion actually coated on the support is not unduly reduced.

Preferably those methods of coating will be employed in which there is no run-back of emulsion to the coating head, i.e. methods in which the quantity of emulsion passed by the coating head is strictly metered to that required to give the desired coating thickness. Moreover, it is important that at all times the quantity of prepared emulsion waiting to be coated should be the minimum possible. For this reason so-called "slab-coating" is preferred. The method normally provides a small surplus of emulsion which is recirculated and it may therefore be provided that any increase in the overflow rate is electronically detected and the information fed back to control the coating speed. In this way it is arranged that any increase in overflow automatically increases coating speed and therefore the rate of pick-up of the emulsion, so that the overflow is immediately compensated.

Alternatively, various methods whereby the prepared

emulsion is extruded on to the support may be employed.

It has been found that, by employing the method of this invention for the coating of the red-sensitive layer in the production of a colour film which, as normally prepared, has a Weston speed of about 10, it is possible to obtain film of identical colour characteristics but a Weston speed of 60 to 80.

The following example will serve to illustrate the invention:

Example

A silver halide emulsion containing 188 gms. of silver and 350 gms. of gelatin is spectrally sensitised to the red end of the spectrum during its manufacture by the addition of 600 mls. of a 1:2000 solution of 3:3'-dimethyl - 6:6' - dimethoxy - 9[1:5 - dimethyl - 2 - phenyl-3-oxo pyrazolinyl (4)] thiacarbocyanine bromide: 260 gms. of gelatin and 100 mls. of wetting agent are added and after adjustment of the pH to 7.4 the total bulk is made up to 11,000 gms. The colour former solution, which is the additive described in this example, contains 310 gms. of gelatin and 170 gms. of colour former (to form a cyan image) added as a 5% solution of the sodium salt of 1-hydroxy-2-naphthoyl-stearylamine-4-sulphonic acid. After adjustment of its pH to 7.4 the solution is diluted to a total bulk of 11,000 gms. The two solutions thus compounded have approximately equal viscosities measured as 10 cps. at the temperature of coating, 35.5° C.: this equality of viscosity assists mixing: owing to the interaction of the colour former with the gelatin of the emulsion the viscosity of the mixed solutions rises to 18 cps.

The emulsion and colour former solutions are held in vessels thermostatically controlled at the coating temperature and each is fed into similar metering pumps driven at the same speed from a motor driven variable speed gear box so that although the ratio of the mixing of the two fluids is invariable yet the total flow can be adjusted to meet the requirements of coating. The metering pumps are of conventional design. The two metered flows are then fed into the mixing cylinder.

A suitable mixing chamber is illustrated in the accompanying drawing. It consists of a small squat form cylinder 1 mounted vertically: a thick rotating spindle 2 runs centrally down the cylinder having its lower bearing on the base and its upper bearing on a baffle 11 across the cylinder. Attached to the spindle at its lower end is a small plastic covered magnet 3 which serves a dual purpose; primarily it is the drive, this being achieved magnetically from outside by means of the rotating magnet 4 driven from the gear box 5 and the motor 6. Secondarily it serves as the first stage of mixing as the two liquids are fed into this section of the cylinder from opposite entry ports 7 and 8. This method of driving obviates the need for glands thus reducing the chances of contamination or the introduction of air bubbles. The upper portion of the cylinder 1 is divided by baffles 9 into segments, the liquid flow between the segments being at the periphery of the baffles 9. Mounted on the spindle and running closely between the baffles 9 are discs 10, the mixing being brought about by the rotation of the discs 10, the upward flow of liquid taking place at the outer edges of the baffles 9 where it is sheared by the rotating discs 10. These may operate at 100 r.p.m. The mixed liquid then flows through holes in the baffle supporting the upper bearing, through the exit port 12 at the top of

the cylinder 1, and then direct to the coating head where it is continuously coated on film base at a coating speed of 10 feet per minute. The coated film passes, a few seconds after being coated, through a chill-box which sets the emulsion, and then through a drying chamber.

On examining a 500 foot length of the coating by sensitometric exposures through a filter passing only the longer wavelengths of the spectrum, no changes in speed were found, the whole coating being quite uniform.

In other experiments not employing the method described above but working with the same final emulsion, a gradual loss of red-sensitivity was found amounting to log E 0.30 over the period of time that would be taken in coating a 500 foot length (50 minutes).

Whilst the invention has been described with particular reference to the case where the additive is a colour coupler, it will be understood that it is applicable to any case where the additive is one which tends to reduce the sensitivity of the liquid emulsion over a period of time. Thus it also includes the case where the additive is a dyestuff, e.g. an azo dyestuff, which has such an effect.

What we claim is:

1. In a method of producing colour photographic materials which comprises: preparing a color sensitized silver halide emulsion by adding a color sensitizing dye to a silver halide emulsion; thereafter adding to the sensitized emulsion a color coupler the presence of which tends to reduce the sensitivity of the emulsion, and thereafter applying the resulting composition to a support layer as a coating thereon; the improvement which comprises: deferring the addition of the color coupler solution to the color sensitized emulsion until the color sensitized emulsion has been brought to the site at which it is to be applied to the support layer and thereupon admixing the color coupler with the color sensitized emulsion; and promptly thereafter applying the freshly formed admixture to the support layer whereby the support is coated with the minimum possible time delay between the time of admixing and the time of coating, and the coating is set and dried with the minimum delay.

2. In a method of producing colour photographic materials which comprises: preparing a color sensitized silver halide emulsion by adding a color sensitizing dye to a silver halide emulsion; thereafter continuously adding to the sensitized emulsion a color coupler the presence of which tends to reduce the sensitivity of the emulsion, and thereafter continuously applying the resulting composition to a support layer as a coating thereon; the improvement which comprises: deferring the continuous addition of the color coupler solution to the color sensitized emulsion until the color sensitized emulsion has been brought to the site at which it is to be applied to the support layer and thereupon continuously admixing the color coupler with the color sensitized emulsion; and promptly thereafter continuously applying the freshly formed admixture to the support layer whereby the support is coated with the minimum possible time delay between the time of admixing and the time of coating, and the coating is set and dried with the minimum delay.

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