of like commodities by nearly 48 million dollars; in 1893 the two movements were practically balanced, while in 1905 exports exceeded imports by 117 million dollars.

The principal articles comprising this exportation of 143 million dollars' worth of iron and steel during the last calendar year, stated in the order of their magnitude, were: Miscellaneous machinery, 25 million dollars; builders' hardware, saws and tools, 12½ millions; pipes and fittings, 8 1/3 millions; electrical machinery, 7 2/5 millions; steel rails, 7 1/3 millions; wire, 7 millions; sewing machines, 6½ millions; locomotives, 5 3/5 millions; and typewriters, 5 millions of dollars. Other important items of less than 5 million dollars' value each were: Billets, ingots, and blooms, 4¼ million dollars; structural iron and steel, 4 1/3 millions; sheets and plates, 3 2/5 millions; pumps and pumping machinery, 3 3/4 millions; nails and spikes, 2½ millions; cash registers, 2 1/5 millions; firearms, 1¼ millions; castings, 1 3/5 millions; steel bars or rods, 1½ millions; printing presses, 1½ millions; shoe machinery, 1 2/5 millions; bar iron, 1¼ millions; and stoves, 1 million dollars; these twenty-three classes supplying in 1905 fully 80 per cent of the total exportations of iron and steel.

As to the destination of iron and steel exports, South America and Mexico are the best customers for our steel rails; Canada, the United Kingdom, and Australia take most of our builders' hardware; electrical machinery goes chiefly to Canada, Japan, Mexico, and Great Britain; sewing machines, chiefly to the United Kingdom, Germany, Argentina, Mexico, and Holland; most of our locomotives to Japan; typewriters, chiefly to the United Kingdom and other European countries, while in lesser amounts the various products of iron and steel are sent to practically every known section of the civilized world.

PINACHROMY AND PINATYPE: NEW PROCESSES OF COLOR PHOTOGRAPHY.*

By H. A. METZ.

DR. E. KOENIG, of the Farbwerke, vorm. Meister, Lucius and Brüning, has developed two new processes in color photography which are known respectively as "pinachromy" and "pinatype." They are not only of interest to the student of chemistry and physics, but are a distinct and important advance toward the reproduction of objects in their natural colors.

In pinachromy, three colloid films are successively superimposed and colored by the action of light on certain sensitive chemical preparations with which the films are coated, thus making a true colored photograph. The process has met with considerable success abroad, and is based on the light sensitiveness of the leuco-bases of the organic dyestuffs. While many of these leuco-bases, for instance those of the safranines, are so oxidizable that they cannot be isolated in a free state, there are others, like the leucomalachite green, which can be easily produced, and are comparatively stable. These more permanent leuco-bases, when exposed for some time to light, become strongly colored.

Dr. Koenig examined all the leuco-bases at his command, but found that when exposed to light, either by themselves, or in gelatin coatings, none of them gave results of the desired strength or brilliancy. Subsequently he selected colloid as the support, and thus obtained the desired increase in sensitiveness, the leuco-bases, in the presence of colloid, becoming strongly oxidized after a comparatively short exposure. This increased reaction he attributed to the presence of the nitric acid groups in the nitro-cellulose, and upon further experiment found that, like nitro-cellulose, all nitric acid esters would react. The nitrous acid esters, on the contrary, and the isomeric nitro derivatives of the aliphatic and aromatic hydrocarbons proved ineffective. The nitrosamines showed reactions similar to, but weaker than, those of the nitric acid esters. It is of interest that the light sensitiveness of the mixture of nitrocellulose with the leuco-bases is considerably reduced by the presence of urea or of antipyrine. This would seem to point to the fact that the leuco-bases are oxidized by nitrogen oxides, which separate from the colloid. While nitrocellulose is by no means the most effective of such compounds, still greater sensitiveness resulting from the admixture of leuco-bases with the nitric acid esters of glycerol, glucose, or mannitol, it is the most suitable compound, as it acts at the same time as the film and as the support for the picture. The light sensitiveness of the mixture of nitrocellulose and the leuco bodies can be considerably increased by the addition of nitroamannitol.

Blue pictures are produced with leucocyanine, which is *o*-chlorotetraethylaminotriphenylmethane; green with leucomalachite green, or with *m*-nitro- or *m*-aminotetraethylaminotriphenylmethane; red with *p*-leuco-aniline, or leuco-rhodamine; violet with hexamethyl-*p*-leucaniline (the leuco-base of Violet B crystals), and yellow with leucofluorescein or leucoflavaniline. The fixing of the picture is effected with dilute organic acids, of which monochloroacetic acid is the best; acetic acid or di- or tri-chloroacetic acids cannot be used.

The practical application of this process is as follows: A sheet of paper is coated with the blue colloid mixture and exposed under its corresponding negative. When the blue picture appears sufficiently strong, it is fixed in a 10 per cent solution of chloroacetic acid, washed, coated with a thin gelatin film, and dried. This gelatin film serves to protect the first colloid coating from dissolving when the second coating is put

on. The dry blue picture is then covered with the yellow colloid mixture and exposed under its corresponding negative, care being taken that the pictures register accurately. After exposure it is fixed, washed, and dried, and the yellow picture produced. The final red picture is obtained in a corresponding manner. On account of the complete transparency of these very thin films, and the brilliancy of the colors produced, the prints appear very uniform. The fastness to light of pinachromy pictures is naturally not absolute, but the dyestuffs used are relatively fast. The poorest is the blue, but even this surpasses the "blue prints" (cyanotypes) in fastness. The quantity of the leuco bodies necessary is extremely small; hence pictures composed of the three-color films cost but a trifle more to produce than ordinary gum or pigment prints.

In pinatype, the second process, on the other hand, a single gelatin film is so treated that a succession of paper prints may be obtained from the colored plate as often as desired. This makes pinatype especially adapted to three-color work, and it is now being carefully tested for this purpose. A bichromated gelatin plate is exposed to light under a photographic negative, and the undecomposed bichromate is removed by washing. Pinatype dyes have the property of dyeing the unhardened gelatin very strongly, whereas the hardened portions are either not colored at all or very slightly. If moist paper, coated with specially prepared gelatin, is now brought into intimate contact with the gelatin layer, colored by means of a pinatype dye, in a short time a colored paper picture with all the half-tones is obtained, which appears strongly colored on those parts not affected by light, while the most exposed parts remain white. From this it is evident that in order to obtain a positive picture the bichromated gelatin layer must be exposed under a diapositive. The facility with which enlarged copies can be made is especially important for three-color photography, as the direct production of large-sized plates in three colors offers many technical difficulties. By this process the negatives can be enlarged directly, whereby all the details are much better preserved than when an enlarged negative has to be prepared from the original negative. The print plates for pinatype, which are not sensitive to light, are steeped with the film side uppermost, for three or four minutes, in a sensitizing solution (2 grammes of chromic acid dissolved in 110 cubic centimeters of water) in shaded daylight or lamplight. The solution must not be warmer than 20 deg. C. Any bubbles of air should be removed with the finger or a brush. A great number of plates may be sensitized, one after the other, in the same bath. After the plates have been sensitized, they are well drained and dried in a dark and not too warm place, free from dust. The sensitized plates keep much longer than sensitized pigment paper, and preserve their qualities completely for two or three weeks. The diapositives to be copied are laid in a frame with the film side in contact with the film side of a sensitized print plate. The exposure time for a print plate is about the same as that for colloid paper. Electric arc light is just as good as direct sunlight for copying. After copying, the pictures should be distinctly seen in brown color on a yellow background. The print plate is now washed in running water until all undecomposed chromic acid has been removed. Usually washing is complete in ten minutes. The plates may now be dried or placed directly in the dye solution. The well-washed print plate, either dry or moist, which corresponds to the red filter negative, is steeped in the blue dye solution composed of 5 grammes of "pinatype blue" dissolved in 250 cubic centimeters of water, and the dish rocked from time to time. The first dyeing takes about 15 minutes. The plate is then washed and rinsed until the water running off from it is no longer colored. It should have the appearance of the diapositive full of detail, with almost transparent whites and intense shades. When the dyed plate is finished, a piece of transfer paper of the size of the plate is softened in cold water, all air bubbles being removed, until the paper has become completely pliable and fully stretched. The paper is now attached to the plate, preferably under water, with the film side against the film side of the printed plate, and both removed from the bath, at the same time draining off the excess of water by a gentle motion of the hand. The plate is then laid upon a table, paper uppermost, and protected with a piece of oiled silk or the like, and the paper firmly smoothed over with a rubber squeegee, from the middle outward, using moderate pressure. The operation is similar to that in the pigment process. When the paper adheres satisfactorily it is covered with a damp sheet and a glass plate, in order to prevent evaporation, and the whole allowed to stand 10 to 15 minutes, if desired, under a light weight. At the end of this time the picture will be found transferred to the paper with sufficient strength. The paper is now removed and hung up to dry. The print plate is now again placed for about five minutes in the dyebath, rinsed, and the picture again transferred to paper as above directed. These operations may be repeated as often as desired. By repeated immersion in the dyebath the print plate becomes darker. Nevertheless, the prints from the plate are quite uniform, as only the exterior surface of the dyed plate has action on the paper. The dyed plates may be kept for any length of time after use, and can be again employed after a fresh immersion in the dyebath. The dyeing of the print plate corresponding with the green filter negative is done in the same manner. For the dye-bath 5 grammes of "pinatype red" are stirred with a little water to a paste, and then 3 to 5 cubic centimeters of concentrated ammonia solution added. Sufficient ammonia must be used to

completely dissolve the dye to a clear deep red solution. After about five minutes the solution is diluted with cold water to 250 cubic centimeters. After the red plate has been washed free from the excess of dyestuff, the blue picture is softened in water and laid under water upon the red print plate. The operation is carried out in the same way as before described, the blue picture being easily shifted under water, so as to exactly correspond to the red print plate. When the adjustment is complete, the paper is held firmly against the plate with suitable clamps, leaving the film free. The film is then withdrawn, water again run over the plate, and the paper pressed firmly down with the squeegee. It is allowed to stand for 10 to 15 minutes, and the paper then removed from the plate. About 30 minutes should be allowed for the first immersion of the print plate, corresponding to the blue filter negative, in a dyebath composed of 5 grammes of "pinatype yellow" dissolved in 200 cubic centimeters of hot water; for subsequent immersions, five to ten minutes. The yellow transfer upon the blue and red picture takes about 30 minutes. It is advisable to moisten the superimposed damp sheet well in order to prevent the films adhering to each other. To increase the picture's fastness to light, and to harden the gelatin layer, the paper is now immersed for about one to two minutes in a fixing bath of 2 grammes of fixative chromium salt and 100 cubic centimeters of water. After fixing, the picture is washed for about five minutes in clean water and hung up to dry.

The principal advantages of pinatype lies in the use of print plates, which are prepared in a simple manner with the aid of light, allowing the preparation of a large number of paper copies therefrom by a purely mechanical process, without further recourse to light. The print plates can be kept and used again at any time, without the aid of light, for the preparation of paper copies. In consequence of the intensity of the pinatype dyestuffs and the immunity from spoiled pictures, pinatypes are very cheap. Pinatypes are extremely fast to light. A three-colored pinatype is not composed of different films. A single thin film carries all of the colors, which therefore blend harmoniously.

OZOBROME PHOTOGRAPHY.

By CHAPMAN JONES, F.I.C., F.C.S., Etc.

THIS curious word is derived from "ozone" and "bromine," though it indicates a process with which ozone has nothing to do, and bromine very little. It is a method recently patented by Mr. Thomas Manly (who, a few years ago, introduced the ozotype process), by which a bromide print is made to furnish one or several carbon prints. This means that the facility of making a bromide print either by contact or enlarging methods, necessitating only a few seconds' exposure to artificial light, may be combined with the advantages of carbon or pigment prints with their permanency and the wide choice of colors that they permit. Indeed, the new method presents notable advantages as compared with the ordinary carbon process, for not only is daylight unnecessary for the exposure, but the print is not laterally reversed though there is no double transfer, and in one modification no transfer at all. The principles involved are very simple. The bromide print consists of a metallic silver image in a gelatin film. Silver is in many cases a very efficient reducer, and by bringing into contact with it a pigmented gelatin film sensitized with a bichromate, the silver, directly or indirectly, reduces the chromate, much as exposure to light would, to a chromium compound which renders the gelatin insoluble.

The practical details run on the following lines: A bromide print, which may be an old one, but must have been thoroughly washed, is soaked in a formaline solution for a few minutes to harden the gelatin, and washed. The carbon tissue or "pigment plaster" that is to be used is soaked till limp in a solution that contains an alkaline bichromate, ferricyanide, and bromide, while the bromide print is soaked in water, and the two squeezed together. If one print only is required, after a few minutes the print is plunged into hot water and developed in the same manner as a single transfer carbon print. But if desired, the same bromide print will furnish several carbon prints, by plunging the original with the carbon tissue squeezed to it into cold water, separating them gently, and then treating the carbon tissue exactly as if it had been just exposed to light in ordinary carbon printing. The short contact with the original is equivalent to the otherwise necessary, and often prolonged, exposure to daylight under the negative. The silver of the bromide print is changed into a silver salt, but immersion in an ordinary developing solution reduces it to the metallic state, and so it can be used over and over again. It seems that all carbon tissue is not suitable, and that a specially soluble kind is supplied by the patentee. Full working details will probably be obtainable before this is published, together with modifications and other applications of the process.

This process seems, on the face of it, to have so much to commend it that the essential difference between it and carbon printing by the ordinary methods must not be lost sight of. Carbon printing, as hitherto practised, is a printing-out process, and the charm of a carbon transparency, as well as its reliability for reproduction purposes, lies largely in this fact. Probably no method gives a more exact representation of the negative, for the possibilities of altering the gradation by accident or design are hardly worth consideration. But in the "ozobrome" methods, the result depends upon development in the same sense in which

* Journal of Society of Chemical Industry.