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PROCESS FOR PRODUCING COLOR PRINTS

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Many of the processes for producing prints in natural colors make use of the fact that unhardened gelatin may readily be colored by means of dyestuffs whereas hardened gelatin cannot be so colored at all, or only with difficulty. This fact is also utilized in the said processes in order to obtain paper prints in natural colors in a very simple manner by imprinting this imbibed dyestuff image on to gelatin printing paper. The disadvantage of yielding only very impure whites which attends these printing processes was only removed when the hardened gelatin was used as a printing matrix, a relief of the tanned gelatin being prepared by dissolving out the unhardened gelatin in warm water. But then the new difficulty arose of making the hardened gelatin, which is inherently dye-repelling, receptive for dyestuffs, which difficulty has not yet been obviated with complete satisfaction in every respect by the methods heretofore known. All these printing processes based on the absorption or imbibition principle, however, entail two great disadvantages, as a result of which their practical use is seriously impaired. In the first place the prints produced by these known methods show imperfect image sharpness owing to the fact that the dyestuff proceeding from the gelatin printing image into the gelatin of the printing paper spreads into the latter, not only vertically, but laterally as well, which leads to blurred and indefinite contours, and in the second place the absorption or imbibition prints, for reason hereinafter stated, show a gradation differing from that of the original image, which is a very serious disadvantage for the production of three-color prints true to nature. For the purpose of avoiding the blurred contours of the image it has been proposed to use particularly hard, and therefore less absorptive, gelatin for the printing paper. This leads to a partial improvement but by no means to a removal of the blur of the print, and, moreover, it also strongly retards the printing speed and renders the use of printing presses essential for the production of uniform prints. It has also been proposed to add to the print gelatin metallic compounds which are dye mordanting mediums such as are usual for fixing dyes in the fabric dyeing art. The addition of such metallic compounds acts pre-eminently so as to harden the gelatin and consequently leads to a lessening of the strong lateral spreading of the dyestuffs; however, the positive and complete fixation of these dyestuffs by this formation of lakes, in which fixation, in the dyeing industry, the fibers themselves play an essential chemical role, could not

be attained in photography, i. e. in conjunction with gelatin. On the contrary, with the metal mordants used in the prior patent specifications referred to a subsequent fixation of the dye image by further chemical treatment baths and a coating of a layer of collodion for protection against the effects of moisture were found to be necessary.

Up till now, the obviation has been unsuccessful of the particularly disadvantageous falsification of the gradation of the print images, which on the one hand is to be attributed to the fact that the imbibed dyestuff is, to a large extent, washed out again from the finest and exceedingly thin, places of the gelatin relief during the necessary washing of the dyed print film before the squeegeeing, and on the other hand to the fact that, during the squeegeeing, the transference of the dyestuff from the printing film into the printing paper is not effected to completion but only to a certain equilibrium stage.

The essence of the present invention is first to fix transiently the dyestuff imbibed by the gelatin relief in a water-insoluble or difficultly soluble form in the relief, so that during the washing away of the adhering dyestuff solution no detail of the colored image is lost, and then to liberate the dyestuff again from the printing relief by a suitable chemical preparation of the printing paper, and to precipitate it instantly, completely and in a permanently water-insoluble form during the transference into the printing paper. All lateral spreading of the dyestuff in the gelatin is avoided by the careful and complete precipitation of the dyestuff during its entry into the gelatin and so that even when soft printing gelatin is used, an absolute image sharpness is produced. Above all, however, the transference of the dyestuff from the print relief into the printing paper is effected according to this invention not just up to a certain equilibrium stage, but the dyestuff, in consequence of the strong chemical affinity in combination with its complete precipitation, is drawn over into the printing paper completely and with extraordinary speed. It is only by this complete transference of the dyestuff image attained in this way in accordance with the process that the completely unchanged gradation of the print image can be produced; in the imbibition processes, known hitherto, transference of the dyestuff attainable only up to a certain equilibrium stage leads to a different printing of the half-tones as compared with the color depths, and consequently to dull print images owing to the equalization of contrasts. Since, moreover, ac-

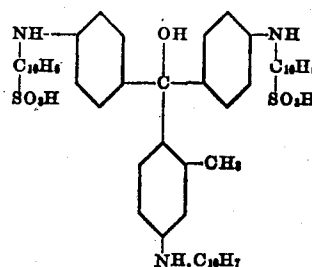
cording to the present invention the gelatin relief absorbs a quite definite amount of dyestuff up to saturation and this passes wholly into the printing paper owing to chemical combination, perfectly uniform color prints are always produced, which is now done for the first time and could not be attained by the usual imbibition processes, even by maintaining constant time of contact between the gelatin relief and the printing paper.

As fixing agents which precipitate the dyestuffs in the gelatin in such a thorough and permanently insoluble manner, as the present process requires and as is not possible by the common dyestuff fixing agents, are named barium salts for acid and particularly sulphonic acid dyestuffs. Preferably these are added to the layer of the printing paper in insoluble, finely divided form, e. g. as barium carbonate, and the printing relief, colored e. g. with diamine fast blue FF, brilliant pure blue Schultz 541 or pure diamine blue FF, carmoisine red, Schultz 163 is squeegeed on. The dyestuff, which enters into the printing paper, is there immediately precipitated as insoluble baryta salt owing to chemical interaction. If the gelatin relief of the part color component, which has been colored with carmoisine D Schultz 193, is squeegeed on to this blue image in accurate register therewith the red image mikado gold-colored Schultz 10 is produced. By transference of the yellow part color image mimosa yellow Schultz 198 in an analogous manner a complete colored image of perfect sharpness is then obtained. If the printing is effected with basic dyestuffs, for instance red Schultz 569, auramine yellow Schultz 494 dyestuff-drawing mordant compounds e. g. cuprous iodide, silver iodide, copper thio-cyanate, may be added to the gelatin of the printing paper. These firmly hold the basic dyestuffs and prevent their lateral spreading, since they form a water-insoluble addition compound with them. These addition-compounds (such as have been proposed already by Arx in his British Patent No. 245,163) possess the drawback that they are non-transparent, so that they cannot be used for projection-pictures in color, and they possess the further drawback that they do not precipitate the dyestuffs in an insoluble manner, so that they pass into the baryto-layer when drying the paper image of the gelatin. According to the present invention these two drawbacks are avoided in that these dyestuff mordant images are bathed in sulphurated phenols known by the trade-name "Katanol" or in dyestuff-precipitating complex acids such as phosphotungstic acid or phosphormolybdic acid $\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O} \cdot 11\text{MoO}_3$ and hereafter the mordant-members are fixed by hyposulphite of soda. The said dyestuff precipitating agents may also, according to the present invention, be introduced directly into the gelatin, since they form with this transparent, strongly dye-drawing compounds, so that the basic dyestuffs penetrating into the gelatin are precipitated instantly by these compounds as perfectly insoluble, transparent dyestuff compounds.

When chemically preparing the printing paper and in order to promote the correct working thereof, the dyestuff imbibed in the gelatin printing relief is chemically combined with the same or temporarily transformed into an insoluble or difficultly soluble form.

When using acid dyestuffs, the free dye acids of which are insoluble, it is sufficient to introduce the colored relief into a weak acid bath without rinsing, whereupon the dyestuff in the relief is precipitated as dye acid.

The dye acid is precipitated fully water-insoluble by means of diluted hydrochloric acid for instance from the aqueous solution of brilliant pure blue.



The gelatin-free places can then be cleansed by washing with water without there being any fear of the slightest loss of the dyestuff absorbed by the gelatin. Before squeegeeing the relief prepared in this manner on to the printing paper the latter is bathed in a solution which converts the insoluble form of the dyestuff into a soluble form. In the case of dye acids, for example alkali baths such as diluted soda or borax solution are employed herefor.

When using basic dyestuffs for printing these are converted in an analogous manner, by bathing the gelatin relief in alkali, into the insoluble color base, or else are converted into an insoluble compound which readily splits up when bathed e. g. in picric acid. In the case of basic dyestuffs, however, the chemical activity of gelatin itself may also be employed for temporarily rendering the dyestuff in the gelatin relief insoluble, by specially choosing basic dyestuff for dyeing purposes having a chemical affinity towards albumin bodies which is so high that they enter into a more stable chemical combination with the gelatin itself, dyestuffs suited for this purpose being for instance crystal-violet Schultz 516 or fuchsine Schultz 512.

I claim:

1. Process for producing color prints by transferring a dyestuff from a printing matrix to an image ground, which consists in using the printing matrix in the form of a colloid relief, imbibing said relief with a dyestuff, temporarily binding the imbibed dyestuff in a difficultly soluble manner by treating said relief with compounds precipitating the dyestuff, placing in contact said relief with the image ground prepared with a chemical agent for releasing the dyestuff from said relief so that it may pass to the image ground and is precipitated in said image ground in a water-insoluble form.

2. Process for producing color prints by transferring a dyestuff from a printing matrix to an image ground, which consists in using the printing matrix in the form of a colloid relief, imbibing said relief with a dyestuff of an affinity for albuminous substances, temporarily binding the imbibed dyestuff in a difficultly soluble manner by treating said relief with compounds precipitating the dyestuff, placing in contact said relief with the image ground prepared with a chemical agent for releasing the dyestuff from said relief so that it may pass to the image ground and is precipitated in said image ground in a water-insoluble form.

3. Process for producing color prints by transferring a dyestuff from a printing matrix to an image ground, which consists in using the printing matrix in the form of a colloid relief produced by a gelatin emulsion containing substances

capable of binding a dyestuff in a difficultly soluble manner, imbibing said relief with a dyestuff of an affinity for said substances, temporarily binding the imbibed dyestuff in a difficultly soluble manner by treating said relief with compounds precipitating the dyestuff, placing in

contact said relief with the image ground prepared with a chemical agent for releasing the dyestuff from said relief so that it may pass to the image ground and is precipitated in said image ground in a water-insoluble form.

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