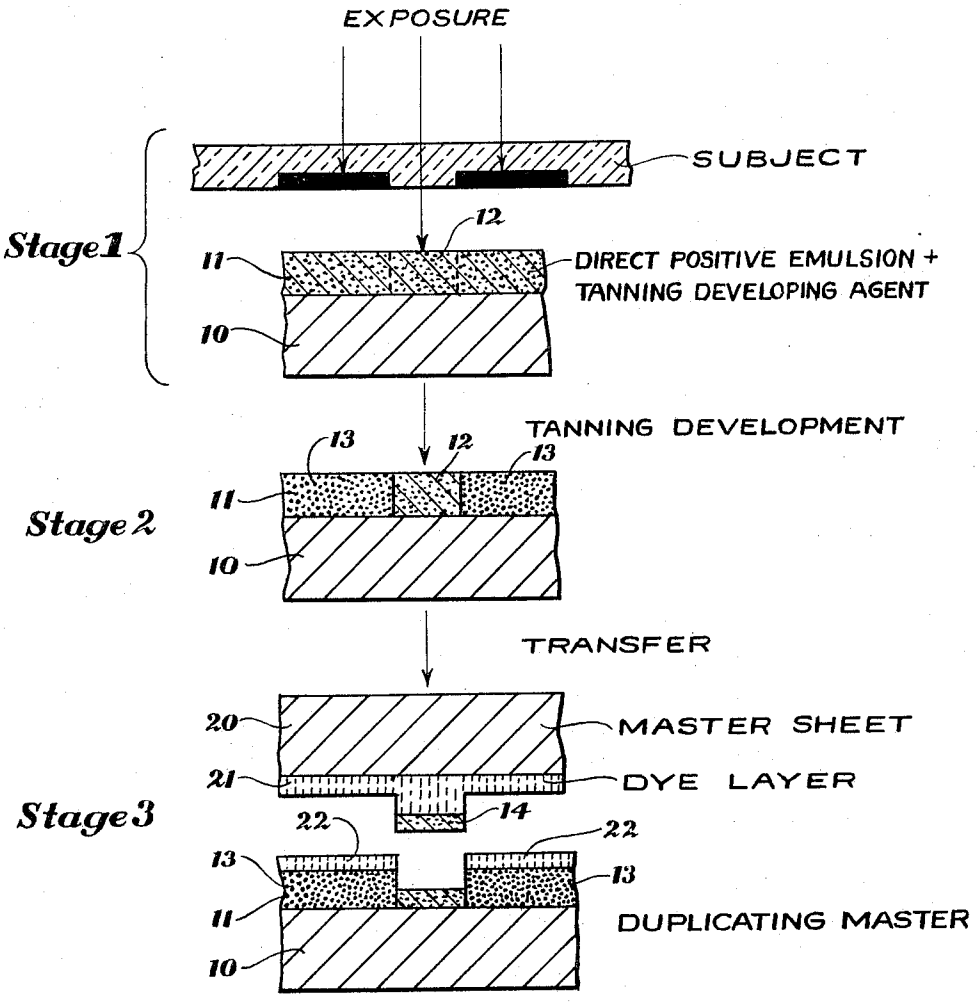
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PHOTOGRAPHIC SPIRIT DUPLICATING PROCESS

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PHOTOGRAPHIC SPIRIT DUPLICATING PROCESS

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This invention relates to photography and more particularly to the use of photographic materials and processes in the preparation of printing elements for use in the spirit duplicating process.

In the usual spirit duplicating process, a duplicating master is prepared by typing, drawing or otherwise forming a design on a sheet of paper while the sheet is in contact with the inked or colored surface of a spirit duplicating master sheet with the result that the coloring material of the duplicating master sheet is transferred to the back of the paper sheet in the form of a laterally reversed image. Copies are prepared from the resulting duplicating master by moistening the surface of the sheet with a liquid, usually alcoholic, which partially dissolves the coloring material forming the design on the sheet and when a copy sheet is pressed against the duplicating master a portion of the colored design transfers to the copy sheet producing a positive image of the original thereon. When the subject matter to be reproduced by the spirit duplicating process exists in a printed, typed or other form, such as line or half-tone subject matter, so-called two-tone subjects, a simple process is desired so as to avoid re-typing or re-drawing the subject. It has been found that the photographic procedures of my invention described below dispense with typing or other manual procedures for reproducing the subject matter in the spirit duplicating process.

Some of the experimental work leading to the prefection of my invention, in a process similar to that described in the Staehle et al. U.S. Patent 2,898,852 granted August 11, 1959, involved preparing a photographic element having a layer of dye on a support and an unhardened silver halide emulsion layer containing a gelatin tanning silver halide developing agent coated over the dye layer. After exposure of the emulsion to the subject, it was activated with alkaline solution so as to develop the exposed emulsion and tan it in the developed regions. Thereafter the emulsion was placed into contact with an absorbent sheet after which the emulsion and sheet were stripped apart to remove the unhardened emulsion areas and to bare the underlying dye layer. The resulting product was printed with limited success in the spirit duplicating process. The process was deficient for several reasons, i.e. the unhardened emulsion areas were not always completely removed, therefore the underlying dye layer was not uniformly bared, also since the dye was present in recessed areas of the sheet, the dye did not print uniformly, also since the dye was present in a layer underlying the emulsion layer, this prevented the use of reflex exposure methods.

In the processes of my invention these obstacles are overcome by a process in which a sensitive element is provided such as described in the Yutzy and Yackel U.S. Patents 2,596,756 and 2,716,059 including a substantially unhardened gelatino silver halide emulsion containing a gelatin tanning silver halide developing agent such as 3,4-dihydroxydiphenyl (4-phenyl catechol) exposing the emulsion to the subject and treating with alkaline solution to develop the silver halide which has been rendered developable by the exposure, with the result that the emulsion becomes hardened or tanned in the developed areas, the remaining areas being unhardened. While the emulsion is still moist from development, it is then pressed into contact with a spirit duplicating master sheet and after a few seconds stripped away with the result that the unhardened emulsion areas are transferred to the surface of the duplicating master sheet described hereinafter, and portions of the dye layer of the sheet are transferred to the emulsion layer in the regions of the tanned image areas. The resulting duplicating master having colored material affixed to the tanned emulsion areas can then be printed as usual in the spirit duplicating process.

My invention can be adapted to the production of either negative or positive copies of a subject depending upon whether a negative or direct positive emulsion is used. That is, in a negative-positive process, when a negative emulsion containing tanning developing agent is used, the result of exposure and development with the alkaline solution is to form a negative tanned-gelatin-and-silver-image in the regions of exposure to which tanned image the dye of the spirit master sheet adheres and is used to produce negative copies of the subject in the spirit duplicating process. In a positive-positive process, when a direct-positive emulsion is used, the exposure and alkaline development steps result in a positive tanned-gelatin-and-silver-image being formed in the unexposed regions, consequently the dye layer adheres to the tanned regions and provides positive prints of the subject in the spirit duplicating process. The latter process is described in more detail in the examples, particularly in conjunction with the drawings.

In the negative-positive process, an emulsion coating can be provided as described in Example 1 of U.S. Patent 2,596,756 containing substantially unhardened gelatin, silver halide and a dispersion of a tanning developing agent such as 3,4-dihydroxydiphenyl, 2,5-dihydroxydiphenyl, 2,3-dihydroxydiphenyl, etc., or if desired, as described in U.S. Patent 2,716,059 a non-tanning silver halide developing agent such as 4-methoxy-1-naphthol may be used in conjunction with the tanning developing agent.

In the positive-positive process, an unhardened direct-positive emulsion such as an unhardened internal latent image emulsion containing a gelatin tanning silver halide developing agent, or an unhardened solarizing emulsion containing a gelatin tanning silver halide developing agent may be used.

The direct-positive emulsions to which the tanning developing agents are added are unhardened emulsions having well-known sensitometric properties, the unexposed (positive) portions rather than the exposed (negative) portions of which are developed during the initial development with a silver halide developing agent.

The direct-positive emulsions include (1) unhardened solarizing silver halide emulsions and (2) unhardened internal latent image silver halide emulsions forming the latent image mostly inside the silver halide grains.

The solarizing direct-positive silver halide emulsions are silver halide emulsions which have been effectively fogged either chemically (by non-hardening compounds) or by radiation, to a point which corresponds approximately to the maximum density of the reversal curve as shown by Mees, The Theory of the Photographic Process, published by the MacMillan Co., New York, New York, 1942, pages 261–297. Typical methods for the preparation of solarizing emulsions are shown by Groves British Patent 443,245, February 25, 1936, who subjected emulsions to Röntgen rays "until an emulsion layer formed therefrom, when developed without preliminary exposure, is blackened up to the apex of its gradation curve"; Szaz British Patent 462,730, March 15, 1937, the use of either light or chemicals such as silver nitrate, organic sulfur compounds and dyes to convert ordinary silver halide emulsions to solarizing direct-positive emulsions; Arens U.S. Patent 2,005,837, June 25, 1935, the

use of nitrate and other compounds in conjunction with heat to effect solarization of the silver halide, and Leermakers U.S. Patent 2,184,013 the use of non-acid optical sensitizing dyes and reducing agents to effect solarization. Kendall and Hill U.S. Patent 2,541,472, February 13, 1951, shows useful solarizing emulsions particularly susceptible to exposure with long wavelength light and initial development to produce the Herschel effect described by Mees above, produced by adding benzothiazoles and other compounds to the emulsions which are fogged either chemically or with white light. In using the emulsions a sufficient reversal image exposure is employed using minus blue light of from about 500–700 mμ wavelength, preferably 520–540 mμ, to substantially destroy the latent image in the sliver halide grains in the region of the image exposure. In these procedures, of course, only non-hardening chemicals are selected for use in fogging the solarizing emulsions.

Conventional silver halide developing solutions can be used to develop a direct-positive image in the solarizing emulsions.

The internal latent image direct positive silver halide emulsions used in the invention are those well known in the art which upon exposure form the latent image mostly inside the silver halide grains, the direct-positive properties of the emulsions being attributable to the crystalline structure of the silver halide grains. That is, a number of authorities in the field of photography have shown that there are imperfections or flaws, in the crystal structure (on the surface or internally) of silver halide which is used in photography, at which flaws the latent image forms by trapping photoelectrons to give development centers. Development, therefore, commences at the sites of these flaws.[1]

Berry, Journal of Applied Physics 27, 636–639 (1956), gives physical evidence based upon convergent-beam X-ray analysis of crystal structure that the silver halide emulsions vary in the number of internal dislocations in the silver halide crystal and that the internal sensitivity is related directly to the number of such dislocations. Other than this, little else is known of the structure of emulsions of the internal latent image type which form the latent image mostly inside the silver halide grains.

Berg et al. J.O.S.A. 31, 385–394 (1941) in discussing the "Latent-Image Distribution" have shown that it is necessary to use a development method in order to distinguish between the surface and internal latent image of silver halide crystals, a "surface developer" (free of silver halide solvent) giving more development to the surface latent image and less of the internal latent image, and an "internal developer" (containing silver halide solvent) being used to develop the internal latent image.

Accordingly, the internal latent image emulsions which form the latent image mostly inside the silver halide grain, are defined as silver halide emulsions, the silver halide grains of which have a crystalline structure such as to cause a test portion of the emulsion upon exposure to a light intensity scale for a fixed time between $\frac{1}{100}$ and 1 second and development for 3 minutes at 20° C. in the following internal type developer:

	Grams
Hydroquinone	15
Monomethyl-p-aminophenol sulfate	15
Anhydrous sodium sulfite	50
Potassium bromide	10
Sodium hydroxide	25
Sodium thiosulfate (crystals)	20

Water to 1 liter.

[1] Journal of Photographic Science. "Photographic Sensitivity," text of lecture given on July 1, 1957, by J. W. Mitchell; 6, No. 3 (1958), and
Fundamental Mechanisms of Photographic Sensitivity. Proceedings of a symposium held at the University of Bristol in March 1950. Published in 1951 in London by Butterworths Scientific Publications. "Some Chemical Factors in Emulsion Sensitivity," by W. G. Lowe, J. E. Jones and H. E. Roberts.

to give a maximum density at least 5 times the maximum density obtained when the equally exposed silver halide emulsion is developed for 4 minutes at 20° C. in the following surface developer:

p-Hydroxyphenylglycine	10
Sodium carbonate (crystals)	100

Water to 1 liter.

An internal latent image emulsion, as described on pages 296 and 297 of Mees' "The Theory of the Photographic Process," 1942, is especially useful for the process of the invention.

Most of the internal latent image emulsions are silver bromo-iodide emulsions of high iodide content, preferably containing at least 10%–20% of iodide. Burton's emulsion is an emulsion of this type, having a silver iodide content of approximately 40% of the content of silver halide. It is not absolutely essential, however, for the emulsion to contain silver iodide.

An internal latent image emulsion made as described in Davey and Knott U.S. Patent 2,592,250 granted April 8, 1952, may also be used according to the invention. This emulsion is prepared by first forming in the absence of ammonia and in one or more stages silver salt grains consisting at least partly of a silver salt which is more soluble in water than silver bromide, subsequently converting the grains to silver bromide or silver bromoiodide and if the silver iodide content of the emulsion is less than 6% calculated on the total silver halide, treating such grains with an iodine compound to bring the silver iodide up to at least 6%, ripening preferably in the absence of ammonia and then either washing out some of the soluble salts or washing out the whole of the soluble salts, followed by the addition of soluble salts such as soluble chloride or bromide. An example of an emulsion made in this way is as follows:

SOLUTION NO. 1

		At 40° C.
Inert gelatine	grams	20
KCl	do	20
Water	cc	560

SOLUTION NO. 2

		At 45° C.
KCl	grams	100
Water	cc	520

SOLUTION NO. 3

		At 45° C.
$AgNO_3$	grams	195
Water	cc	520

SOLUTION NO. 4

		At 45° C.
KBr	grams	160
Kl	do	40
Water	cc	500

Run Solutions Nos. 2 and 3 simultaneously into Solution No. 1 in a vessel, taking 90 seconds to do this. Then ripen for 1 minute at 45° C. Next add Solution No. 4, then ripen for 20 minutes at 45° C. Next add 235 grams of inert gelatine (dry). Then ripen at 45° C. for 15 minutes during which time the gelatine dissolves. Set and shred the emulsion and then wash until free from all soluble bromide and then add about 150 cc. of 10% solution of KCl (by weight), and then add water to make 3½ liters.

As shown by various patents, e.g. Knott et al. U.S. 2,456,953, December 21, 1948, Falleson U.S. 2,497,875, February 21, 1950 and Ives U.S. Patents 2,563,785, August 7, 1951 and 2,588,982, March 11, 1952 the internal latent image direct-positive emulsions so defined may be to yield direct positive images by employing a fogging

exposure during development or by the use of fogging developer solutions. The Ives patents mentioned may be referred to for useful hydrazine-containing fogging silver halide developing compositions in which the developing agent should be a primary aromatic amino silver halide color developing agent. The color developing agent is not especially critical and may be selected from the well known primary aromatic amino compounds.

The internal latent image emulsions can be processed as described in the Cowden et al. U.S. Patent 2,835,575 using a hydrazine compound such as p-(β-methylsulfonamidoethyl)phenylhydrazine in the developing solution.

Direct-positive emulsions especially useful in the process of the invention are prepared by chemically fogging silver halide emulsions particularly silver chloride emulsions or silver cholorobromide emulsions predominately silver chloride, by means of non-hardening reducing agents for silver halide, i.e. silver halide reducing agents free of hardening action upon gelatin. Direct-positive emulsions are known which have been chemically fogged with formaldehyde and other compounds which harden the emulsions thereby rendering them unsuitable for use in the processes of the invention. However, when the non-hardening reducing agents such as the following are used, the emulsions remain unhardened throughout the development step of the process. Suitable non-hardening silver halide reducing agents are, for example, polyamines having the general formula

$$H_2N(RNH)_nRNH_2$$

wherein R is an alkylene chain containing from 2 to 4 carbon atoms and *n* is positive integer of from 1 to 5, spermine and water-soluble salts thereof, water-soluble formaldehyde sulfoxalate salts, water-soluble stannous salts, formamidine sulfinic acid and water-soluble salts thereof, the emulsion also containing a gelatin tanning silver halide developing agent.

These reducing agents are used in the emulsions in the manner described below in relatively large amount compared to the amount of other addenda such as sensitizers which are used in emulsions, the quantity depending upon the activity of the particular compound as a fogging agent for silver halide and the procedure used in fogging the emulsions with the particular compound. Thus, in the case of stannous chloride, from about 5 mg. to 20 mg. of $SnCl_2 \cdot H_2O$ per mole of silver halide produces a useful direct positive emulsion. However, the smaller amounts usually require longer heating of the emulsion to produce a sufficient fog level, e.g. at the 5 mg. level the emulsion may be heated about 20 minutes at 80° C., whereas at 20 mg. level about 1 minute at 80° C. The optimum quantity of other silver halide reducing compounds can be ascertained by simple experiment. Other organic and inorganic compounds which are active reducing agents for silver halide can be used insofar as they do not harden the gelatin vehicle of the emulsion.

If desired, a desensitizer of silver halide well known in the art can be added to the mentioned emulsions fogged with the non-hardening reducing agents, for example, the desensitizers disclosed by the Stewart et al. U.S. patent application Serial No. 812,847 filed May 13, 1959, including heavy metal salts such as mercury salts and rhodium salts and organic desensitizers containing at least one benzene ring containing at least one nitro substituent. Typical of such organic desensitizers are benzotriazole compounds containing a nitro substituent on the benzene ring of the benzotriazole nucleus, e.g., 5-nitrobenzene-1,2,3-triazole, 4-nitrobenzo-1,2,3-triazole, etc. (including their halogen substituted derivatives, such as 5-chloro-, 6-chloro-, etc.). Another group of chemical desensitizers comprise a class of dyes known as styryl dyes which contain at least one nitro substituent attached to a benzene ring. Other chemical sensitizers include safranine dyes. Anthraquinone dyes containing a sulfoalkylaminosulfone radical can also be used to desensitize the photographic silver halide emulsions. Typical compounds are:

Mercuric chloride
Triammonium hexachlororhodite
3,5-dinitrobenzhydrazide
5-nitrobenzo-1,2,3-triazole
4-nitro-6-chlorobenzotriazole
2,3-dimethyl-6-nitrobenzothiazolium p-toluenesulfonate
2-phenylbenzo-1,2,3-thiadiazolium bromide
N,N'-decamethylene-bis(quinoxalinium)perchlorate
Methylene blue chloride
1-methyl-2(p-nitrostyryl)-6-ethoxyquinolinium p-toluenesulfonate
2-(p-diethylaminophenyliminomethyl)-1,6-dimethylquinolinium chloride
2-(p-dimethylaminophenyliminomethyl)-3-ethylbenzothiazolium ethosulfate
Phenosafranine (chloride)
Pinakryprol green (chloride)
1,3-diamino-5-methylphenazinium chloride
3-methyl-2-bias(phenylazo)methylene benzothiazoline

Typical compounds are those having at least one nitro group attached to a benzene nucleus, said compound being selected from the class consisting of benzothiazole, quinoline, indolenine, benzotriazole, and rhodanine compounds and their alkyl quaternary salts. These compounds are especially useful in the direct positive emulsions which have been produced by use of the nonhardening silver halide reducing compounds mentioned. A suitable amount of de-sensitizer to use is about 0.15 to 3.0 grams per mole of silver halide in the emulsion.

The substantially unhardened gelatin emulsions have a hardness of the order described in U.S. Patent 2,716,059, i.e. they are not substantially harder than would be the case of gelatin containing about 0.7 gram of dry formaldehyde per pound of gelatin freshly coated. The emulsions are coated on a variety of supports including ordinary paper or water-resistant paper substantially free of gelatin hardener and especially good results are obtained by coating the emulsions on paper which has been coated with polyethylene the surface of which has been bombarded with corona discharge to control the adhesion of the emulsion thereto.

It has been mentioned that in the process of the invention the developed emulsion is placed in contact with a duplicating master sheet, whereupon portions of the dye layer of the master sheet adhere to the developed areas of the emulsion and the undeveloped areas of the emulsion adhere to the dye layer. This result can be obtained to some extent by use of commercially available spirit duplicating master sheets such as Columbia Ready Master (Columbia Ribbon Company) or Ditto Royalty Carbon (Ditto Company) but most of the commercial master sheets are useless in the process. One reason for this appears to lie in the fact that some of these sheets carry a waxy coating on the outer surface which prevents adherence of the emulsion to the sheet particularly in the developed regions of the emulsion. For the best results the master sheet should carry a layer of an alcohol-soluble coloring material such as an alcohol-soluble dye, e.g. Crystal Violet, mixed with a moisture absorptive pigment such as carbon black or titanium oxide. The moisture absorptive pigment serves to impart hydrophilic properties to the dye layer with the result that the adherence between the emulsion and dye layer is improved and the unhardened emulsion areas transfer more uniformly to the dye layer with the ultimate result that much sharper prints having higher dye density are obtained with the duplicating process. While the combination of dye and moisture absorptive pigment gives useful results, in a preferred embodiment of the invention, in addition to dye and moisture absorptive pigment, the dye layer contains a dye-fixative which tends to prevent the dye from diffusing to the support such as either a

water soluble aliphatic polyhydric alcohol the alkyl chain of which contains at least 5 carbon atoms, e.g. (1) polyalkylene oxides containing recurring alkylene oxide units containing from 2 to 4 carbon atoms, as in polyethylene, polypropylene and polybutylene oxides having molecular weights of about 200 to 1500, 2-ethyl-1,3-hexanediol or 1,2,6-hexanetriol, or (2) a water soluble alkylarylpolyether alcohol (including sulfonated alkylarylpolyether alcohols) such as sold under the trade names Triton X–100 and Triton X–200 respectively, etc., and particularly one of these water soluble dye-fixing agents (1) or (2) in combination with (3) compounds accelerating the spirit extraction of dye in the duplicating process, i.e. substantially water insoluble carboxylic acids and esters containing at least 12 carbon atoms, e.g. oleic acid, ethyl oleate, ethyl laurate, diethyl sebacate, methyl undecanoate and dibutyl phthalate. Materials (1), (2) and (3) serve to improve the sharpness and density of the prints.

The ratio of pigment to dye can be varied somewhat depending upon the density and number of prints desired; however, optimum results are obtained with about one part of dye to about 0.6 to 2.5 parts of carbon preferably one part of dye to about 1.2 to 1.5 parts of carbon. When the polyalkylene oxides are used, about 3 to 9 grams and preferably 4 to 7.5 grams per 100 grams of total dye and pigment such as carbon can be used.

The dyes used in the spirit duplicating master sheet can be those commonly used in the spirit duplicating process and include, for example, Methyl Violet, Malachite Green, Fuchsine, Eosine, Auramine, Methylene Blue and 3,3,3',3'-tetramethyl - 1,1' - diethyl - indodicarbocyanine iodide.

The coloring materials used in the master sheet include not only dyes such as mentioned but also initially colorless materials capable of being converted to colored materials during the spirit duplicating printing operation, that is, the couplers and diazonium salts of diazotype process can be used in the unhardened emulsion layer, the dye layer or in the copy sheets with the result that when alkali is supplied in the spirit duplicating printing step the coupler and diazonium salt couple to yield azo dye prints. Thus, when the diazonium salt is present in the dye master the coupler can be in the copy sheet and alkali in the alcohol solution, or both the coupler and alkali may be present in the alcohol solution, or the coupler may be in the sensitive emulsion and the alkali in the alcohol solution or the coupler and alkali may be present in the emulsion. Similarly, the coupler can be in the dye master when the diazonium salt is in the copy sheet and alkali is in the alcohol solution. Accordingly, a useful dye master contains diazonium salt or coupler together with the moisture-absorbing pigment and also if desired, a polyalkylene oxide.

The alkaline developing solution used to initiate development of the emulsion may contain organic or inorganic alkali, e.g. alkali metal hydroxide or carbonate such as sodium or potassium cabonates and in addition, may contain gelatin softening agents such as urea or formamide to aid in control of the emulsion hardness during the transfer step.

The usual alcoholic fluids are used in the spirit duplicating process of the invention and include the lower alcohols such as methyl and ethyl alcohols and mixtures thereof.

The accompanying drawings show in greatly enlarged cross-sectional view the appearance of representative elements used in the process of preparing a duplicating master image for use in the spirit duplicating process. As shown therein, in Stage 1, a sensitive element composed of a support **10** such as paper, cellulose ester, etc., and a direct positive emulsion layer **11** containing a gelatin tanning silver halide developing agent, is exposed to a subject, the exposure having effect upon area **12**. Thereafter, tanning development is effected by application of an alkaline solution to the exposed layer resulting in the tanned gelatin and silver images being formed in areas **13** of layer **11** as shown in Stage 2. Thereafter, as shown in Stage 3, a duplicating master sheet composed of a paper or other support **20**, and the dye layer **21** containing dye and moisture-absorptive pigment, is pressed into contact with the freshly developed emulsion of Stage 2 with the result that portions of the dye layer adhere strongly to the tanning developed areas **13** of the emulsion layer, and the unhardened emulsion of area **12** adheres to the dye layer. Accordingly, when, after a few seconds, the emulsion layer and master sheet are stripped apart, the dye images **22** become detached from the dye layer and remain adhered to the tanned emulsion images **13**, thereby producing a duplicating master. At the same time the emulsion image **14** separates from the emulsion layer **11** and remains adhered to the dye layer. The application of alcohol solution and the dye images **22** in the spirit duplicating process causes portions of the dye to transfer to the copy sheet and provide a positive reproduction of the subject having high definition. Of course, when the initial emulsion of layer **11** of Stage 1 contains a negative emulsion, a negative-positive process is in operation and positive prints are obtained from a negative subject such as a film negative.

The following examples will serve to illustrate my invention:

Example 1

A direct positive emulsion was prepared by using a gelatin-silver chloride emulsion containing one mole of silver chloride, adjusting the pH to 8.5 with dilute sodium hydroxide solution and adding 10 mg. of $SnCl_2 \cdot 2H_2O$ in 5 cc. of methyl alcohol. The emulsion was then heated to 80° C. for seven minutes then cooled to 40° C. and the pH adjusted to 6.0 with dilute sulfuric acid. Then, 680 grams of the 4-phenyl catechol dispersion below were added, 650 grams of 10% gelatin solution, 100 cc. of 15% saponin solution and 2075 cc. of water. The mixture was then coated on a polyethylene coated paper support which had been electron bombarded with, e.g. corona discharge until the desired adhesion of the emulsion was obtained.

As shown in the drawings, the resulting emulsion coating **10** on the support **11** was exposed to a line positive in area **12** then activated for about 40 seconds with a 4% solution of $Na_2CO_3 \cdot H_2O$ containing 5% urea to develop the emulsion. The resulting developed direct positive emulsion now containing tanned gelatin and silver images **13** and residual unhardened emulsion in area **12** was then pressed into contact with the Duplicating Master Sheet A below having the dye layer **21**, contact was maintained for a few seconds during which time the dye layer became strongly adhered to the emulsion layer. The two elements were then stripped apart with the result that the unhardened emulsion image **14** remained adhered to the dye layer **21** and portions **22** of the dye layer remained adhered to the tanned emulsion images **13** to provide dye images which were dried then wetted with alcohol solution and printed in a conventional spirit duplicating machine to provide several positive dye prints of the subject.

4-PHENYL CATECHOL DISPERSION

50 grams 4-phenyl catechol in 100 cc. of di-n-butyl phthalate were added with vigorous stirring to 550 cc. of a 10% aqueous gelatin solution containing 50 cc. of 7.5% saponin solution. The mixture was then passed through a colloid mill five times.

DUPLICATING MASTER A

5 grams of Methyl Violet, 20 grams of titanium oxide and 10 cc. of methyl alcohol were treated in a ball mill until a smooth slurry was obtained, following which the mixture was coated on a paper support at a wet thickness of .002 inch and dried.

DUPLICATING MASTER B

A mixture of 9 grams Methyl Violet, 3 grams carbon black pellets, 0.5 cc. of tricresyl phosphate and 10 cc. of methyl alcohol were treated in a ball mill until a smooth slurry was obtained followed by coating on a paper support and drying.

DUPLICATING MASTER C

A mixture of 30 grams carbon black pellets, 60 grams Methyl Violet and 225 cc. of ethyl alcohol were treated in a ball mill for 16 hours to yield a smooth slurry following which 0.5 cc. of tricresyl phosphate was added to 30 grams of the slurry which was then coated on a paper support.

DUPLICATING MASTER SHEET D

A mixture of 900 grams Methyl Violet, 600 grams carbon black, 125 grams Emkapol 150 (a polyethylene glycol having an average molecular weight of about 300), 3500 grams methyl alcohol were treated in a ball mill for 16 hours to yield a smooth slurry which was coated on paper to yield a coating having 0.89 gram of solids per square foot containing 0.5 gram dye, 0.33 gram carbon and 0.06 gram polyethylene glycol per square foot.

DUPLICATING MASTER SHEETS E, F, AND G

The following ingredients were thoroughly mixed:

Methyl Violet Dye	grams	26.5
Molacco Black Carbon pigment	do	40.0
MeOH	ml	191.0

To three such mixtures, 4.0, 5 and 6.0 grams respectively of Carbowax 300 (polyethylene glycol having an average molecular weight of 300) were added and each mixture then coated on paper and dried to provide the master sheets E, F and G.

Example 2

The Duplicating Master Sheet B was used in the process of Example 1 with the result that very sharp images of high density were obtained on each print.

Example 3

The Duplicating Master Sheet C was used in the process of Example 1 thereby yielding several satisfactory prints. In addition, an alkaline activator solution containing 4 percent K_2CO_3 and 2 percent urea, and also a 4 percent solution of potassium carbonate were used in the process with equally satisfactory results, the process being carried out at various temperatures of from 78 to 86° F.

Example 4

The Duplicating Master Sheet D was used in the process of Example 1 except employing a 4 percent potassium carbonate solution containing 2 percent urea with the result that very good prints were obtained in the spirit duplicating process.

Example 5

The Dye Master Sheets E, F and G were used in the process of Example 1 and each gave useful prints; however, sheet G containing the higher level of carbowax yielded slightly less sharp prints than sheets E and F.

Example 6

Master Sheets prepared in the same manner as sheets E, F and G except using 3, 4 and 5 grams of Carbowax 600 respectively per 26.5 parts dye and 40.0 parts carbon, each produced very good prints in the process of Example 1.

Example 7

Duplicating Master Sheets prepared in the same manner as sheets E, F and G, except using 3, 4 and 5 grams of Carbowax 1540 respectively per 26.5 parts dye and 40.0 parts carbon, each produced very good prints in the process of Example 1.

Example 8

A mixture of 300 grams methyl violet dye, 200 grams carbon black, 1200 grams ethyl alcohol and 300 grams of water were treated in a ball mill for 16 hours to yield a smooth slurry which was coated on map overlay paper to yield 1.5 grams of solids per square foot. This was utilized as a control Duplicating Master Sheet 8.

DUPLICATING MASTER SHEET 8A

Same as Sheet 8 but also containing 1.1 grams of Triton X–100 as the dye fixative and 1.1 grams of dye-extraction accelerator oleic acid per 100 grams of the above slurry.

DUPLICATING MASTER SHEET 8B

Same as Sheet 8 but also containing 1.5 grams of 1,2,6-hexanetriol as the dye-fixative and 2.0 grams of the dye-extraction accelerator diethyl sebacate per 100 grams of the above slurry.

DUPLICATING MASTER SHEET 8C

Same as Sheet 8 but also containing 1.5 grams of 1,2,6-hexanetriol as the dye-fixative and 2.5 grams of the dye-extraction accelerator diethyl sebacate per 100 grams of the above slurry.

DUPLICATING MASTER SHEET 8D

Same as Sheet 8 but also containing 2.5 grams of 1,2,6-hexanetriol as the dye fixative and 1.85 grams of the dye-extraction accelerator diethyl sebacate per 100 grams of the above slurry.

It was found that when Sheet 8 was used in the process of Example 1 useful prints were obtained from the fresh sheet but some density was lost after prolonged storage of Sheet 8.

It was found that Duplicating Master Sheets 8A to 8D, even after prolonged storage, produced prints of excellent sharpness and density. Experimentation has shown that, when used with the above type of dye-carbon slurry, the dye-fixative 1,2,6-hexanetriol is best used at levels of from 1.0 gram to 4.0 grams, with the optimum level of 1.5 grams, per 100 grams of the above slurry. The dye-fixative Triton X–100 is best used at levels of from 0.5 to 2.0 grams, with the optimum level of 1.0 gram, per 100 grams of the above slurry. The dye-extraction accelerator diethyl sebacate is best used at levels of from 0.5 gram to 10.0 grams, with the optimum level of 2.5 grams, per 100 grams of the above slurry. The dye-extraction accelerator oleic acid is best used at levels of from 0.5 gram to 2.0 grams, with the optimum level of 1.1 grams, per 100 grams of the above slurry.

In a similar photographic process involving simultaneous transfer from two layers in contact, negative and positive copies of high contrast can be produced simultaneously by developing an unhardened incorporated developer emulsion layer to a hardened relief, bringing the emulsion layer into contact with a graphite-coated sheet, stripping the two layers apart, leaving a negative in the coated sheet, and a graphite-intensified, silver-positive, relief image in the matrix. For example, a photographic silver halide emulsion layer containing a tanning developing agent, coated on a waterproof paper or film support, is exposed to a negative original, immersed for a few seconds in an alkaline activator solution, for example, 5% sodium carbonate solution, until the image becomes visible, then rolled into close contact with a coating containing a very thin layer of colloidal graphite, for example, DAG Dispersion No. 41 (Acheson Colloids Company). After 4 or 5 seconds, the sandwich is warmed to about 90–100° F. and stripped apart. The graphite layer adheres only to the tanned image layer while the untanned gelatin from the emulsion layer transfers to the graphite coating. This results in a negative of excellent contrast in the graphite layer and after a warm water rinse, a positive of good quality in the emulsion layer. The graphite remaining on the tanned gelatin of the photographic emulsion layer must be transferred to a paper receiving sheet.

I claim:

1. A method of forming a printing master, adapted to produce direct reading positive copies of a direct reading positive original to be copied in a spirit duplicating process, by the steps comprising:

(1) Photographically exposing to the original to be copied a silver halide emulsion layer to form in said layer a latent photographic image of said original;

(2) Developing said exposed emulsion layer in the presence of a tanning developing agent to form in said layer a developed photographic image of said original, the areas of said layer wherein the silver halide has been developed to a silver image exhibiting greater gelatin hardness than the remainder thereof;

(3) Pressing said exposed and developed emulsion layer while moist from said developing step 2, and with the developed and undeveloped areas thereof intact and in at least substantially coplanar relationship directly against a hectographic dye-containing layer of a hectographic dye sheet, said dye layer being free of protective coating, and

(4) Separating said emulsion layer and dye sheets with simultaneous transfer of a portion of said emulsion layer in the unhardened areas thereof onto said dye sheet and of a portion of the dye-containing layer onto the hardened areas of said emulsion layer.

2. In a process for preparing a spirit duplicating master comprising producing a developable silver halide image in a substantially unhardened supported gelatin-silver halide emulsion layer containing a gelatin tanning silver halide developing agent by exposure to a subject and contacting the developed emulsion layer with the surface of a spirit duplicating master sheet containing coloring material in order to transfer an unhardened gelatin layer imagewise to the surface of the spirit duplicating master sheet, the improvement which comprises developing the silver halide emulsion with an alkaline solution until the master layer containing coloring material adheres only to the hardened emulsion areas and the unhardened emulsion areas adhere to the layer containing coloring material, pressing the resulting developed emulsion layer while moist into contact with the surface of a spirit duplicating master sheet composed of a mixture of an alcohol-soluble coloring material and a moisture absorptive pigment, so that the surface of the master sheet adheres strongly to the surface of the emulsion layer in the region of development of the tanned gelatin and silver image, and the undeveloped regions of the unhardened emulsion layer adheres strongly to the surface of the master sheet, separating said sheet and emulsion layer to obtain an image composed of unhardened emulsion adhered to the surface of the master sheet, and also an image composed of coloring material adhered to the emulsion layer in the regions of the tanned gelatin and silver image and adapted to printing in a separate duplicating process.

3. In a process for preparing a spirit duplicating master comprising producing a developable silver halide image in a substantially unhardened supported gelatin-silver halide emulsion layer containing a gelatin tanning silver halide developing agent by exposure to a subject and contacting the developed emulsion layer with the surface of a spirit duplicating master sheet containing coloring material in order to transfer an unhardened gelatin layer imagewise to the surface of the spirit duplicating master sheet, the improvement which comprises developing the silver halide emulsion with an alkaline solution until the master layer containing coloring material adheres only to the hardened emulsion areas and the unhardened emulsion areas adhere to the layer containing coloring material, pressing the resulting developed emulsion layer while moist into contact with the surface of a spirit duplicating master sheet composed of a mixture of about 1 part of an alcohol-soluble coloring material and 0.6–2.5 parts of a moisture absorptive pigment, so that the surface of the master sheet adheres strongly to the surface of the emulsion layer in the region of development of the tanned gelatin and silver image, and the undeveloped regions of the unhardened emulsion layer adheres strongly to the surface of the master sheet, separating said sheet and emulsion layer to obtain an image composed of unhardened emulsion adhered to the surface of the master sheet, and also an image composed of coloring material adhered to the emulsion layer in the regions of the tanned gelatin and silver image and adapted to printing in a separate duplicating process.

4. In a process for preparing a spirit duplicating master comprising producing a developable silver halide image in a substantially unhardened supported gelatin-silver halide emulsion layer containing a gelatin tanning silver halide developing agent by exposure to a subject and contacting the developed emulsion layer with the surface of a spirit duplicating master sheet containing coloring material in order to transfer an unhardened gelatin layer imagewise to the surface of the spirit duplicating master sheet, the improvement which comprises developing the silver halide emulsion with an alkaline solution until the master layer containing coloring material adheres only to the hardened emulsion areas and the unhardened emulsion areas adhere to the layer containing coloring material, pressing the resulting developed emulsion layer while moist into contact with the surface of a spirit duplicating master sheet composed of a mixture of about one part of an alcohol soluble coloring material, 0.6–2.5 parts of a moisture absorptive pigment, and .004–.056 part of the polyalkylene oxide of molecular weight of about 200 to 1500 the recurring alkylene oxide units of which contain from 2 to 3 carbon atoms, so that the surface of the master sheet adheres strongly to the surface of the emulsion layer in the region of development of the tanned gelatin and silver image, and the undeveloped regions of the unhardened emulsion layer adheres strongly to the surface of the master sheet, separating said sheet and emulsion layer to obtain an image composed of unhardened emulsion adhered to the surface of the master sheet, and also an image composed of coloring material adhered to the emulsion layer in the regions of the tanned gelatin and silver image and adapted to printing in a separate duplicating process.

5. The process of claim 4 wherein the silver halide emulsion is a direct positive silver halide emulsion containing a gelatin tanning silver halide developing agent and the process results in the tanned gelatin and silver image being obtained in the unexposed regions of the emulsion layer and the coloring material adhered thereto is an alcohol soluble dye.

6. The process of claim 4 wherein the silver halide emulsion is a direct positive photographic emulsion comprising a substantially unhardened gelatin-silver halide emulsion strongly fogged throughout by means of a gelatin non-hardening silver halide reducing agent, the emulsion contains a gelatin tanning silver halide developing agent and the process results in the tanned gelatin and silver image being obtained in the unexposed regions of the emulsion layer and the coloring material adhered thereto is an alcohol soluble dye.

7. The process of claim 2 wherein the silver halide emulsion is a direct positive photographic emulsion containing a substantially unhardened gelatin-silver chloride emulsion strongly fogged throughout by means of a gelatin non-hardening silver halide reducing agent of the class consisting of a polyamine having the general formula

$$H_2N(RNH)_nRNH_2$$

wherein R is an alkylene chain containing from 2 to 4 carbon atoms and n is positive integer of from 1 to 5, spermine and water-soluble salts thereof, water-soluble formaldehyde sulfoxalate salts, water-soluble stannous salts, formamidine sulfinic acid and water-soluble salts thereof, the emulsion also containing a gelatin tanning silver halide developing agent and the process results in the tanned

gelatin and silver image being obtained in the unexposed regions of the emulsion layer and the coloring material adhered thereto is an alcohol soluble dye.

8. In a process for preparing a spirit duplicating master comprising producing a developable silver halide image in a substantially unhardened supported gelatin-silver halide emulsion layer containing a gelatin tanning silver halide developing agent by exposure to a subject and contacting the developed emulsion layer with the surface of a spirit duplicating master sheet containing coloring material in order to transfer an unhardened gelatin layer imagewise to the surface of the spirit duplicating master sheet, the improvement which comprises developing the silver halide emulsion with an alkaline solution until the master layer containing coloring material adheres only to the hardened emulsion areas and the unhardened emulsion areas adhere to the layer containing coloring material, pressing the resulting developed emulsion layer while moist into contact with the surface of a spirit duplicating master sheet composed of a mixture of about one part of an alcohol-soluble coloring material, carbon, and .004–.056 part of a polyalkylene oxide of molecular weight of about 200 to 1500 the recurring alkylene oxide units of which contain from 2 to 3 carbon atoms, so that the surface of the master sheet adheres strongly to the surface of the emulsion layer in the region of development of the tanned gelatin and silver image, and the undeveloped regions of the unhardened emulsion layer adheres strongly to the surface of the master sheet, separating said sheet and emulsion layer to obtain an image composed of unhardened emulsion adhered to the surface of the master sheet, and also an image composed of coloring material adhered to the emulsion layer in the regions of the tanned gelatin and silver image and adapted to printing in a separate duplicating process.

9. In a process for preparing a spirit duplicating master comprising producing a developable silver halide image in a substantially unhardened supported gelatin-silver halide emulsion layer containing a gelatin tanning silver halide developing agent by exposure to a subject and contacting the developed emulsion layer with the surface of a spirit duplicating master sheet containing coloring material in order to transfer an unhardened gelatin layer imagewise to the surface of the spirit duplicating master sheet, the improvement which comprises developing the silver halide emulsion with an alkaline solution until the master layer containing coloring material adheres only to the hardened emulsion areas and taining coloring material, pressing the resulting developed the unhardened emulsion areas adhere to the layer conemulsion layer while moist into contact with the surface of a spirit duplicating master sheet composed of a mixture of an alcohol-soluble coloring material, a moisture absorptive pigment, and a water-soluble aliphatic polyhydric alcohol the alkyl chain of which contains at least 5 carbon atoms, so that the surface of the master sheet adheres strongly to the surface of the emulsion layer in the region of development of the tanned gelatin and silver image, and the undeveloped regions of the unhardened emulsion layer adheres strongly to the surface of the master sheet, separating said sheet and emulsion layer to obtain an image composed of unhardened emulsion adhered to the surface of the master sheet, and also an image composed of coloring material adhered to the emulsion layer in the regions of the tanned gelatin and silver image and adapted to printing in a separate duplicating process.

10. In a process for preparing a spirit duplicating master comprising producing a developable silver halide image in a substantially unhardened supported gelatin-silver halide emulsion layer containing a gelatin tanning silver halide developing agent by exposure to a subject and contacting the developed emulsion layer with the surface of a spirit duplicating master sheet containing coloring material in order to transfer an unhardened gelatin layer imagewise to the surface of the spiirt duplicating master sheet, the improvement which comprises developing the silver halide emulsion with an alkaline solution until the master layer containing coloring material adheres only to the hardened emulsion areas and the unhardened emulsion areas adhere to the layer containing coloring material, pressing the resulting developed emulsion layer while moist into contact with the surface of a spirit duplicating master sheet composed of a mixture of an alcohol-soluble coloring material, a moisture absorptive pigment, and a water-soluble alkylarylpolyether alcohol so that the surface of the master sheet adheres strongly to the surface of the emulsion layer in the region of development of the tanned gelatin and silver image, and the undeveloped regions of the unhardened emulsion layer adheres strongly to the surface of the master sheet, separating said sheet and emulsion layer to obtain an image composed of unhardened emulsion adhered to the surface of the master sheet, and also an image composed of coloring material adhered to the emulsion layer in the regions of the tanned gelatin and silver image and adapted to printing in a separate duplicating process.

11. In a process for preparing a spirit duplicating master comprising producing a developable silver halide image in a substantially unhardened supported gelatin-silver halide emulsion layer containing a gelatin tanning silver halide developing agent by exposure to a subject and contacting the developed emulsion layer with the surface of a spirit duplicating master sheet containing coloring material in order to transfer an unhardened gelatin layer imagewise to the surface of the spirit duplicating master sheet, the improvement which comprises developing the silver halide emulsion with an alkaline solution until the master layer containing coloring material adheres only to the hardened emulsion areas and the unhardened emulsion areas adhere to the layer containing coloring material, pressing the resulting developed emulsion layer while moist into contact with the surface of a spirit duplicating master sheet composed of a mixture of an alcohol-soluble coloring material, a moisture absorptive pigment, a water-soluble aliphatic polyhydric alcohol the alkyl chain of which contains at least five carbon atoms, and a member of the class consisting of substantially water-insoluble carboxylic acids and esters thereof containing at least twelve carbon atoms so that the surface of the master sheet adheres strongly to the surface of the emulsion layer in the region of development of the tanned gelatin and silver image, and the undeveloped regions of the unhardened emulsion layer adheres strongly to the surface of the master sheet, separating said sheet and emulsion layer to obtain an image composed of unhardened emulsion adhered to the surface of the master sheet, and also an image composed of coloring material adhered to the emulsion layer in the regions of the tanned gelatin and silver image and adapted to printing in a separate duplicating process.

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