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3,431,108

SILVER COMPLEX DIFFUSION TRANSFER PROCESS

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Claims priority, application Great Britain, Oct. 11, 1965, 42,970/65

U.S. Cl. 96—29

5 Claims

Int. Cl. G03c 5/54, 7/00

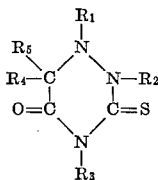
This invention relates to a photographic silver complex diffusion transfer process for producing diffusion transfer images possessing a black or bluish-black image tone and to a material to be used in such process.

The principle of the silver complex diffusion transfer process is described in our British patent specification 614,155, its first Patent of Addition 654,630, and in the German patent specification 887,733. According to this process, a light-sensitive silver halide material is image-wise exposed and thereupon in the presence of a developing substance, a complexing agent for silver halide and a processing liquid brought into contact with an image-receiving material. The exposed parts of the silver halide emulsion layer are developed and do not undergo any further change. The unexposed silver halide is complexed by the complexing agent for silver halide, which is present either in the processing liquid or in the receiving material, and transferred by diffusion into the receiving layer, where it is converted into a silver containing image under the action of developing nuclei. In this way, a positive image of the original appears in the receiving layer after separation of the image-receiving material from the silver halide material.

In addition to the usual development with an organic reduction agent in the presence of photochemical nuclei, finely divided metal particles such as colloidal silver or metal sulphide particles such as cobalt sulphide particles can initiate or catalyse the conversion of the transferred silver complex to a silver containing image in the receiving layer. A disadvantage of the silver complex diffusion transfer process, especially when metal sulphide nuclei are used, is the less agreeable brown image tone of the obtained silver containing diffusion transfer image.

Generally, this disadvantage is counteracted by the addition of a black-toning agent. Usually, this is an organic heterocyclic compound containing thioxo or their tautomeric mercapto groups. A widely used black-toning agent is 1-phenyl-2-tetrazoline-5-thione, which improves the image tone indeed, but at the same time strongly delays the formation of the diffusion transfer image in the image-receiving material, so that a longer contact time is required in order for obtaining sufficiently dense prints. The used amount of this compound has to be kept within specific and rather narrow limits, since too high a concentration of black-toning agent even completely prevents development.

It has now been found that black or bluish-black transfer images are obtained in an accelerated way by carrying out the silver complex diffusion transfer process in the presence of at least one compound corresponding to the following general formula or to a tautomeric structure thereof:



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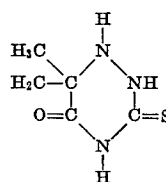
wherein

R₁, R₂, R₃, R₄ and R₅ (the same or different) each represent a hydrogen atom, an alkyl group including a substituted alkyl group, an aryl group including a substituted aryl group, with the proviso, however, that at least one of the substituents R₂ and R₃ represents a hydrogen atom;

R₄ and R₅ may also represent the atoms necessary to complete a carbocyclic ring including a substituted carbocyclic ring.

The following is a non-restrictive list of black-toning agents, which have proved to be particularly suitable for use according to the present invention, and which correspond to the above general formula.

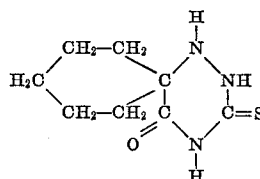
COMPOUND 1



6,6-dimethyl-3-thio-1,6-dihydro-as-triazine-3,5(2H,4H)-dione. Melting point: 248–249° C.

Preparation described by Fusco and Rossi. Gazz. Chim. Ital., 89, 373 (1954).

COMPOUND 2

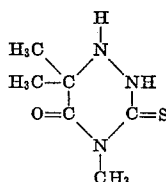


3-thio-1,2,4-triazaspiro[5,5]undecane-3,5-dione.

Melting point: 224° C.

Preparation described by Fusco and Rossi. Gazz. Chim. Ital., 89, 373 (1954).

COMPOUND 3

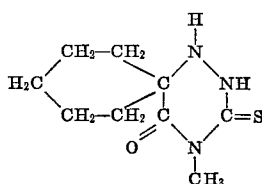


4,6,6-trimethyl-3-thio-1,6-dihydro-as-triazine-3,5(2H,4H)-dione.

Melting point: 190° C.

This compound can be prepared according to preparation 1 as described further hereinafter.

COMPOUND 4

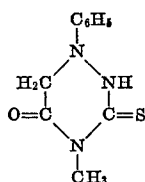


4-methyl-3-thio-1,2,4-triazaspiro[5,5]undecane-3,5-dione.

Melting point: 210° C.

This compound can be prepared according to preparation 2, as described further hereinafter.

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COMPOUND 5

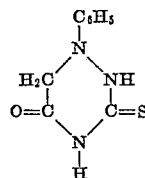


1 - phenyl - 4 - methyl-3-thio-1,6-dihydro-as-triazine-3,5 (2H,4H)-dione.

Melting point: 180–190° C.

This compound can be prepared according to preparation 3, as described further hereinafter.

COMPOUND 6

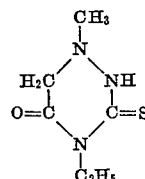


1 - phenyl - 3 - thio-1,6-dihydro-as-triazine-3,5(2H,4H)-dione.

Melting point: 172–173° C.

Preparation described by Busch and Meussdörffer, Ber. 40, 1021 (1907).

COMPOUND 7



1 - methyl - 4 - ethyl-3-thio-1,6-dihydro-as-triazine-3,5 (2H,4H)-dione.

Melting point: 129° C.

This compound can be prepared according to preparation 4 as described further hereinafter.

PREPARATION 1

A. Preparation of the intermediate product 1-(1'-cyano-1'-methyl-ethyl)-4-methyl-thiosemicarbazide

21 g. of 4-methyl-thiosemicarbazide are dissolved in 80 ccs. of a mixture of ethanol and water (1:1). Whilst stirring, the solution, there are successively added at room temperature: 11.5 ccs. of acetic acid, a solution of 13 g. of potassium cyanide in 25 ml. of water and 12.6 ccs. of acetone. The reaction mixture is refluxed for 1 hour. After cooling, the formed crystals are filtered by suction (yield: 34.5 g., melting point: 197–203° C.) and recrystallized from 1600 ccs. of ethanol.

Yield: 25.5 g. of 1-(1'-cyano-1'-methyl-ethyl)-4-methyl-thiosemicarbazide. Melting point: 210° C.

Microanalysis.—Calculated for $C_8H_{12}N_4S$ (molecular weight: 172): C, 42.45; H, 6.87; S, 18.39. Found: C, 41.90; H, 7.03; S, 18.64.

B. Preparation of compound 3

800 g. of the obtained 1-(1'-cyano-1'-methyl-ethyl)-4-methyl-thiosemicarbazide are dissolved in 3300 ccs. of an aqueous hydrochloric acid solution (d.=1.17) and heated for 24 hours at 80° C. On cooling, ammonium chloride crystallizes and is filtered by suction. The filtrate is brought at pH 3–4 by means of 2200 ccs. ammonium hydroxide, whereby 4,6,6-trimethyl-3-thio-1,6-dihydro-as-triazine-3,5 (2H,4H)-dione precipitates together with ammonium chloride. The precipitate is crystallized from water (5500 ccs.).

Yield: 160 g. of 4,6,6-trimethyl-3-thio-1,6-dihydro-as-triazine-3,5(2H,4H)-dione. Melting point: 190° C.

Microanalysis.—Calculated for $C_8H_{11}ON_3S$ (molecular weight: 173): C, 41.65; H, 6.41; S, 18.54. Found: C, 41.92; H, 6.38; S, 18.33.

PREPARATION 2

A. Preparation of the intermediate product 1-(1'-cyano-cyclohexyl-4-methyl-thiosemicarbazide

105 g. of 4-methyl-thiosemicarbazide are dissolved in 400 ccs. of a mixture of ethanol and water (1:1). Whilst stirring the solution at 10° C. there are successively added: 57.5 ccs. of acetic acid, a solution of 65 g. of potassium cyanide in 125 ccs. of water and 98 g. of cyclohexanone. The reaction mixture is refluxed for 2 hours, whilst stirring. After cooling, the crystals formed are filtered by suction and washed with ethanol and ether.

Yield: 189 g. of 1-(1'-cyano-cyclohexyl)-4-methyl-thiosemicarbazide. Melting point: 200° C.

Microanalysis.—Calculated for $C_9H_{16}N_4S$ (molecular weight: 212): C, 50.99; H, 7.61; S, 15.13. Found: C, 51.22; H, 7.84; S, 15.00.

B. Preparation of compound 4

189 g. of 1-(1'-cyano-cyclohexyl)-4-methyl-thiosemicarbazide are dissolved in 1375 ccs. of an aqueous hydrochloric acid solution (d.=1.17) and heated for 24 hours at 80° C. After cooling, the formed precipitate is filtered by suction and washed with water, whereafter it is recrystallized from 3500 ccs. of ethanol.

Yield: 125 g. of 4-methyl-3-thio-1,2,4-triazospiro-5,5-undecane-3,5-dione. Melting point: 210° C.

Microanalysis.—Calculated for $C_9H_{15}ON_3S$ (molecular weight: 213): C, 50.75; H, 7.10; S, 15.05. Found: C, 50.47; H, 7.08; S, 15.05.

PREPARATION 3

70 g. of 1-phenyl-1-ethoxyacetyl-hydrazine hydrochloride are dissolved in 450 ccs. of water. By adding 17.1 g. of ammonium carbonate 1 aq., the base is set free from its hydrochloride whereupon it is extracted with ether. After drying the etheric solution over molecular sieves, a solution of 15.6 g. of methylisothiocyanate in 220 ccs. of ether is added. By evaporation of the ether an oil is left which is dissolved in 75 ccs. of anhydrous ethanol and to which a solution of 11.2 g. of potassium hydroxide in 140 ccs. of ethanol is added whilst cooling at 0° C. A yellow precipitate is formed (39 g.) which is filtered by suction, dissolved in 100 ccs. of water and acidified with acetic acid.

Yield: 35 g. of 1-phenyl-4-methyl-3-thio-1,6-dihydro-as-triazine-3,5(2H,4H)-dione. Melting point: 180–190° C.

Microanalysis.—Calculated for $C_{10}H_{11}ON_3S$ (molecular weight: 221): C, 54.34; H, 5.02; S, 14.51. Found: C, 54.32; H, 4.93; S, 14.55.

PREPARATION 4

45 g. of 1-methyl-1-ethoxyacetyl hydrazine hydrochloride are suspended in 230 ccs. anhydrous ether and whilst thoroughly stirring at 0° C. ammonia gas is introduced. The formed ammonium chloride is removed by filtration. By evaporation of the ether of the filtrate, an oil is left which is again dissolved in 205 ccs. anhydrous ether and this solution is added to a solution of 21.6 ccs. of ethylisothiocyanate in 205 ccs. of anhydrous ether. After stirring for half an hour at room temperature, the ether is evaporated. The residue is dissolved in 100 ccs. of anhydrous ethanol and whilst stirring at 0° C., a solution of 16.2 g. of potassium hydroxide in 190 ccs. of anhydrous ethanol is dropwise added. After stirring for one hour, the ethanol is evaporated. The remaining yellow oil is added to 200 ccs. of water and acidified with acetic acid. The precipitate is crystallized from 50 ccs. of ethanol of 1-methyl-4-ethyl-3-thio-1,6-dihydro-as-triazine-3,5(2H,4H)-dione.

Yield: 13 g. Melting point: 129° C.

Microanalysis.—Calculated $C_6H_{11}ON_3S$ (molecular

weight: 173): C, 41.65; H, 6.41; S, 18.54. Found: C, 41.73; H, 6.29; S, 18.60.

The black-toning agent according to this invention can be present in the processing bath and/or in the image-receiving material. When present in the processing bath, its uses to be in amounts mostly comprised between about 30 and about 1000 mg. per litre of processing bath.

When incorporated into the image-receiving material, i.e. in the image-receiving layer and/or into a water-permeable layer from which it can diffuse in due time to the image-receiving layer (i.e. in a water-permeable layer, which is in working contact with the image-receiving layer) its uses to be preferably in amounts ranging from about 10 to about 300 mg. of black-toning agent per sq. m. of image-receiving material.

The image-receiving material which can be used in a silver complex diffusion transfer process according to this invention, mostly consists of a support e.g. of paper which carries one or more layers, one of which is the image-receiving layer or nuclei-containing layer wherein the diffusion transfer image is formed in the presence of developing nuclei (physical and/or chemical) and/or of substances which are capable of forming developing nuclei with the diffusing complexed silver halide. The image-receiving material can also consist of a mere paper support incorporating constituents such as developing nuclei.

Also an image-receiving material can be used which is composed in such a way that several positive copies of an original can be produced from only one image-wise exposed light-sensitive material. Such an image-receiving material is among others described in our British patent specifications 950,960 and 961,177.

The image-receiving layer can also be applied to the same support as the silver halide emulsion layer. In that case, the image-receiving layer is mostly coated onto a support, e.g. of paper and covered with a non-hardened or slightly hardened light-sensitive silver halide emulsion layer. Such a material is described among others in our British patent specification 654,631. After exposure, development and diffusion transfer of the unexposed complexed silver halide into the image-receiving layer, the exposed and developed unhardened emulsion layer can be removed e.g. by washing away with warm water or by stripping after having been in contact with a sheet of common paper. Between the image-receiving layer and the light-sensitive layer there can also be present a separating layer. In our British patent specification Ser. No. 1,006,292 is described a starch ether separating layer which enables the detaching of the light-sensitive layer as a coherent sheet, by simply bringing the multilayer material into an aqueous rinsing bath after the diffusion transfer image formation.

The light-sensitive material suitable for a diffusion transfer process wherein black-toning agents as described above can be used, may be any light-sensitive silver halide material the exposed silver halide of which is sufficiently rapidly developed and the non-exposed silver halide is sufficiently rapidly complexed for allowing the formation of a diffusion transfer image to take place. Preferably, silver chloride emulsions are used which may contain specific amounts of silver bromide or silver iodide or to which some ingredients may be added in order to obtain the desired emulsion characteristics.

The developing substance(s) can be incorporated into the light-sensitive material and/or into the bath and/or into the image-receiving material. Suitable developing substances are among others: hydroquinone, monomethyl-p-aminophenol sulphate, aminophenol and 3-pyrazolidinone developing substances. These developing substances can occasionally, at least partly be present in the materials used. Thus, hydroquinone together with a bisulphite can be present in the image-receiving material, such as described in our British patent specification Ser. No. 1,000,115. Also combinations of two or more devel-

oping agents can be used successfully, such as the combination of hydroquinone and a 3-pyrazolidinone derivative together in the image-receiving material as described in our British patent specification 1,012,476, and the combination of hydroquinone in the image-receiving material and a 3-pyrazolidinone derivative in the light-sensitive material as described in the Belgian patent specifications 633,674 and 635,813.

The complexing agent forming a soluble complex with the silver halides is preferably an alkali thiosulphate and can be incorporated into the image-receiving material as well as into the processing bath.

Sulphides of heavy metals such as antimony, bismuth, cadmium, cobalt, lead, nickel and silver; heavy metals such as silver, gold, platinum, palladium and mercury, preferably in their colloidal form, and/or other substances which can serve as developing nuclei for the complexed silver halide are mostly incorporated into the image-receiving layer. However, they can also be present in the processing bath. In the latter case, use is made of a light-sensitive and image-receiving material with a specific composition. Such diffusion transfer process with developing nuclei and/or compounds capable of forming such nuclei present in the processing bath has among others been described in our British patent specification Ser. No. 1,001,558 and in the Belgian patent specification 635,811.

In many cases it is favourable to counteract the fog formation in the exposed silver halide emulsion layers by using a fog-inhibiting agent. This fog-inhibiting agent e.g. can be present in the light-sensitive silver halide material and/or in the processing bath.

All the ingredients such as developing substances, complexing agents for silver halide, alkali, developing nuclei and the like which are necessary in a silver complex diffusion transfer process can be incorporated into the light-sensitive and/or image-receiving material used so that occasionally common water can be used as processing liquid. A such like process is described in the Belgian patent specification 612,103.

Particulars concerning the exposing and developing apparatus that can be used as well as the silver complex diffusion transfer process in general and the materials suitable therefor, can be found in "Progress in Photography," vol. I, 1940-1950, pp. 76, 77 and 140; vol. II, 1951-1954, pp. 156-157; vol. III, 1955-1958, pp. 24-36 and in the patent literature cited therein.

A diffusion transfer process wherein use is made of black-toning agents as described in this invention, yields diffusion transfer images of a very satisfactory bluish-black to black colour.

Moreover, the black-toning agents to the present invention possess a very important advantage over the known black-toning agents. Indeed, if they are used in the developing bath, they keep this bath clear even after frequent use. It is known that during the diffusion transfer process sometimes finely divided metallic silver is formed in the developer and that after some time this black silver sludge begins to deposit onto the transport parts of the developing apparatus. This involves the disadvantageous consequence that after some time the diffusion transfer copies show black spots. This disadvantage is completely avoided by adding compounds according to the present invention to the developer, which compounds prevent said silver sludge from being formed. At the same time, an additional amount of black-toning agent, occasionally one different from these according to the present invention, may be present in the image-receiving material as well as in the light-sensitive silver halide material.

The following examples illustrate the invention, without limiting, however, same hereto.

Example 1

An image-receiving material is prepared by coating a

paper support with a layer from the following coating composition:

Gelatin	g	40
Sodium thiosulphate 5 aq.	g	35
Colloidal nickel sulphide	mole	1.28 10^{-3}
Solution of Compound 2 in ethanol (0.7%)	ccs	100
Aqueous formaldehyde 20%	ccs	5
Sandozol (trade name for a sulphonated organic oil marketed by Sandoz A.G. Basel, Switzerland)	cc	1
Water to	ccs	1000

This suspension is coated in such a way that 1 litre covers 13 sq. m.

A silver chloride emulsion paper containing per sq. m. 1.35 g. of silver chloride is exposed while being in contact with an original to be reproduced, whereupon it is led together with the above-mentioned image-receiving material in the usual way through a developing bath of the following composition:

Sodium sulphite	g	75
Sodium hydroxide	g	10
Potassium bromide	g	1
Hydroquinone	g	16
1-phenyl-3-pyrazolidinone	g	1
Water to	ccs	1000

On leaving the developing bath, both materials are pressed together and after a contact period of 20 seconds separated from each other. Contrary to the brown image-tone obtained when an image-receiving material which does not contain the above-mentioned black-toning agent is used, an image with completely neutral image-tone is obtained in the receiving layer.

Example 2

An image-receiving material is prepared by coating a paper support with a layer from the following coating composition:

Gelatin	g	40
Sodium thiosulphate 5 aq.	g	30
Colloidal silver sulphide	mole	1.64 10^{-4}
Solution of Compound 5 in ethanol (0.7%)	ccs	100
Aqueous formaldehyde (20%)	ccs	5
Sandozol (trade name)	cc	1
Water to	ccs	1000

This suspension is coated in such a way that 1 litre covers 13 sq. m.

By means of a light-sensitive material as described in Example 1, a diffusion transfer image is produced in this image-receiving material in the same way as described in said Example 1, and this image has a completely neutral image tone.

The same neutral image tone is obtained when using Compound 2 instead of Compound 5.

Example 3

An image-receiving material is prepared by coating a paper support with a layer from the following coating composition:

Gelatin	g	40
Sodium thiosulphate 5 aq.	g	30
Colloidal silver sulphide	mole	1.64 10^{-4}
Ethanol	ccs	100
Aqueous formaldehyde (20%)	ccs	5
Sandozol (trade name)	cc	1
Water to	ccs	1000

This suspension is coated in such a way that 1 litre covers 12 sq. m.

A silver chloride emulsion paper containing per sq. m. 1.35 g. of silver chloride is exposed while being in contact with an original to be reproduced, whereupon it is led together with the above-mentioned image-receiving

material in the usual way through a developing bath as described in Example 1 but which, moreover, contains 330 mg. of Compound 1.

Contrary to the brown image tone obtained when a bath which does not contain the above-mentioned black-toning agent is used, an image with completely neutral image tone is obtained in the receiving layer.

The same neutral image tone is obtained when the Compound 1, present in the developing bath is replaced by a same amount of one of Compounds 2, 3, 4 or 5.

Example 4

An image-receiving material is prepared by coating a 90 g./sq. m. paper support in a ratio of 20 sq. m./l. with a layer from a suspension of the following composition:

Water	ccs	800
Gelatin	g	40
Sodium thiosulphate 5 aq.	g	48
Aqueous sodium sulphide (10%)	ccs	2.5
Aqueous cobalt nitrate (10%)	ccs	13
Solution of 1-phenyl-2-tetrazoline-5-thione in ethanol (1%)	ccs	5
Aqueous formaldehyde (20%)	ccs	5
Sandozol (trade name)	cc	1
Water to	ccs	1000

A silver chloride emulsion paper containing per sq. m. 1.35 g. of silver chloride is exposed while being in contact with an original to be reproduced, whereupon it is led together with the above-mentioned image-receiving material through a developing bath of the following composition:

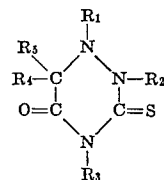
Sodium sulphite	g	75
Sodium hydroxide	g	10
Potassium bromide	g	1
Hydroquinone	g	16
1-phenyl-3-pyrazolidinone	g	1
Sodium thiosulphate 5 aq.	g	3
Water to	ccs	1000

When about 60 diffusion-transfer copies are produced, a black sludge begins to deposit in the processing bath. This sludge formation increases according to whether more diffusion-transfer copies are produced. The diffusion-transfer copies obtained with the aid of a processing bath containing said sludge show black spots.

If on the contrary a processing bath is used with the same above-mentioned composition but which contains moreover 50 mg./litre of Compound 3 or of Compound 4 this bath remains completely clear and can be used until complete exhaustion without silver sludge being formed.

We claim:

1. Photographic silver complex diffusion transfer process according to which a positive image of an original is obtained by development of an image-wise exposed light-sensitive silver halide emulsion layer and diffusion of non-developed complex silver halide from the emulsion layer into an image-receiving material where the complexed silver halide is converted in the presence of development nuclei into a silver-containing image, wherein said process is carried out in the presence of at least one compound corresponding to the following general formula or to a tautomeric structure thereof:



wherein:

each of R_1 , R_2 , R_3 , R_4 and R_5 is hydrogen, alkyl or aryl, with the proviso, however, that at least one of the substituents R_2 and R_3 is hydrogen; R_4 and R_5 may

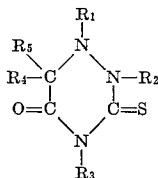
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also represent the atoms necessary to complete a carbocyclic ring.

2. Photographic silver complex diffusion transfer process according to claim 1, wherein the compound defined is present in at least one water-permeable layer of the image-receiving material.

3. Photographic silver complex diffusion transfer process according to claim 1, wherein the compound defined is present in the processing bath.

4. Image-receiving material for use in a silver complex diffusion transfer process, comprising an image-receiving layer and containing in at least one water-permeable layer at least one compound corresponding to the following general formula or to a tautomeric structure thereof:

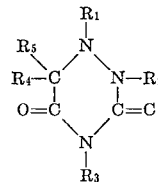


wherein:

each of R_1 , R_2 , R_3 , R_4 and R_5 is hydrogen, alkyl or aryl, with the proviso, however, that at least one of the substituents R_2 and R_3 is hydrogen; R_4 and R_5 may also represent the atoms necessary to complete a carbocyclic ring.

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5. Processing bath for use in a silver complex diffusion transfer process and which contains at least one compound corresponding to the following general formula or to a tautomeric structure thereof:



wherein:

each of R_1 , R_2 , R_3 , R_4 and R_5 is hydrogen, alkyl or aryl, with the proviso, however, that at least one of the substituents R_2 and R_3 is hydrogen; R_4 and R_5 may also represent the atoms necessary to complete a carbocyclic ring.

References Cited

Fusce and Ross, *la Gazzetta Chimica Italiana*, p. 373, 1954.

NORMAN G. TORCHIN, *Primary Examiner*.

J. P. BRAMMER, *Assistant Examiner*.

U.S. Cl. X.R.

96—52, 76

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

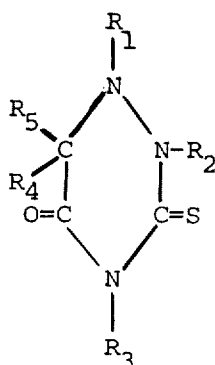
Patent No. 3,431,108

March 4, 1969

Jozef Frans Willems et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 7, line 12, "that I litre" should read -- that 1 litre --.
Column 8, line 5, "complex" should read -- complexed --. Column 10, lines 5 to 10, the formula should appear as shown below:



Signed and sealed this 7th day of April 1970.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents