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54 A color-developer sheet for carbonless copying.

57 A color-developer sheet or set for carbonless copying comprising, in combination, microcapsules containing an electron-donative, colorless organic compound and an activated clay capable of developing a color upon absorption of said organic compound, characterised in that a coating liquid is used comprising an activated clay in solid particulate form which has been admixed in advance with sodium silicate and optionally one or more other dispersants.

A COLOR-DEVELOPER SHEET FOR CARBONLESS COPYING

This invention provides a color-developer sheet for carbonless copying, and more particularly such a color-developer sheet characterized in that a coating liquid is used which results from the use of activated clay in solid particulate form which has been in advance admixed with sodium silicate and optionally other dispersants.

Carbonless copying papers are known as disclosed for example in U.S. Patents No. 2,712,517, No. 2,800,457 and No. 2,730,457. Such carbonless copying paper utilizes microcapsules containing a solution of an electron-donative, non-adsorptive, reactive colorless organic compound (hereinafter referred to as "color-former") and an electron-acceptive, reactive, adsorptive material (hereinafter referred to as "color-developer").

Microencapsulation is effected by means of coacervation, interfacial polymerization, in situ polymerization and other processes. Color-formers include malachite green lactone, crystal violet lactone, benzoyl leuco methylene blue, rhodamine B lactam, 3-dialkylamino-7-dialkylamylfluoran, 3-methyl-2,2-spiropi(benzo[f]-chromene) and the like.

Color-developers include solid acids such as acid clay, activated clay, attapulgate, zeolite, bentonite and the like; an organic group of phenolic resins such as p-tert-butylphenol resin, p-phenylphenol resin, p-octylphenol resin and the like; organic compounds such as succinic acid, tannic acid, malonic acid, gallic acid and the like, or metal compounds thereof; and aromatic carboxylic acids such as benzoic acid, salicylic acid, substituted salicylic acids,

naphthoic acid, diphenic acid and the like, or metal compounds thereof. Typical examples in the usual practice are activated clay phenolic resins and substituted salicylic acids. Phenolic resins and substituted salicylic acids are adequate for high concentration sheet coating but give rise to poor ink absorptivity. These two color-developers have another drawback that due primarily to chemically synthesized substances, they are susceptible to degradation or decomposition of the printed marks under sunlight which would in turn fade away. Inorganic activated clay is superior in ink absorptivity and inexpensive. However, such activated clay color-developer is disadvantageous in that a coating liquid prepared therefrom is liable to become gelled in high concentrations, with ultimate difficulty in sheet coating, and that sheets of paper coated with low-concentration coating liquids involve blanket smear (piling) at the time of printing.

Activated clay used as the color-developer is, as disclosed in Japanese Patent Publications No. 41-2373, No. 41-7622 and No. 42-8811, about $200 \text{ m}^2/\text{g}$ or greater in surface area and prepared by treating acid clay or similar types of clay with a mineral acid to elute acid-soluble alumina, iron and other basic components.

Activated clay, even if mixed with zinc, magnesium and other salts, may be used successfully. An X-ray analysis shows that activated clay is amorphous, relatively large in surface area and characteristically different from ordinary paper coating pigments. When dispersed in water, activated clay requires a greater amount of water to complete the dis-

persion due to its shape, surface activity and other factors.

Kaolin clay typical of paper coating remains fluid in concentrations of 70% and above when dispersed in water, whereas activated clay becomes viscous and gelled in concentrations of about 45%. A strong demand now prevails for high-concentration coating liquids from the point of view of productivity and energy-saving. Activated clay is difficult to process for such high-concentration coating liquids for the reasons already stated. An air-knife coater process is therefore currently employed using low-concentration coating liquids.

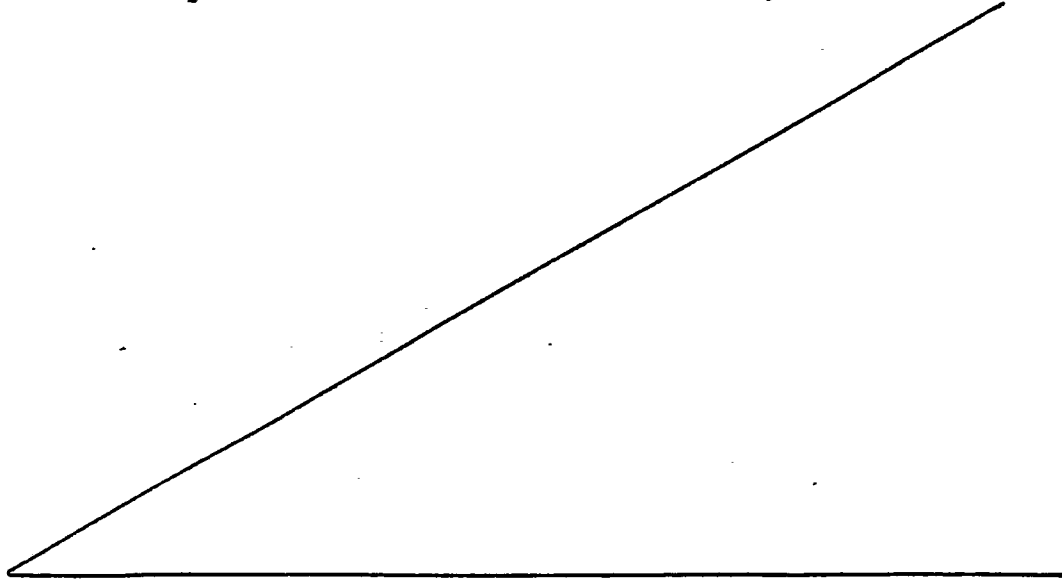
It is therefore an object of the present invention to provide a color-developer sheet for carbonless copying which is coated with a high-concentrations, less viscous, highly fluid coating liquid and which is satisfactory in blanket smear at the time of printing.

It has now been found that the use of the above coating liquid makes it possible to improve dispersability and fluidity of activated clay in water and lower the viscosity and hence control the amount of the coating to be applied in high concentrations. Coating operation may be facilitated, and energy-saving accomplished.

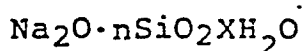
The color-developer sheet produced shows good surface quality, smoothness and smudge resistance (against blurry spots caused by rubbing encapsulated surfaces) and free from blanket smear at the time of printing.

Activated clay used in the present invention may be prepared by treating acid clay with an acid, to be then e.g. washed with water, dried and pulverized. Generally

the sodium silicate and other dispersant if any may be mixed with the clay by various methods. For example after the clay is treated with acid and washed with water, the dispersant may be added and mixed into and with it as aqueous solution. Alternatively after the clay is treated with acid and before drying the dispersant is added and mixed in a powder state. Alternatively again, after drying, the dispersant is added, mixed and crushed in powder state. In another method, after crushing, the dispersant in powdered state is added and mixed, but the invention is not restricted to these methods only. As other dispersants that can be combinedly used with sodium silicate inorganic dispersants such as sodium tripolyphosphate, sodium hexametaphosphate, sodium pyrophosphate and so on and organic dispersants based on carboxylic acids (e.g. acrylates), and maleic acid particularly (e.g. styrene maleic anhydride salt and so on), and sulfonic acid compounds (such as naphthalene sulfonate and so on) can be used.

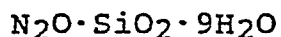
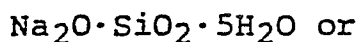


Sodium silicate as used in the invention is known as a water glass and includes kinds dissolved in water and others in particulate form. Typical examples commercially available are sodium silicate No. 1, No. 2 and No. 3, which are represented by the formula



where n is about 2 for No. 1, about 2.5 for No. 2 and about 3 for No. 3.

Sodium meta-silicate is represented by the formula



Any of these is effective as a dispersant and more effective, the greater the mol ratio of Na_2O .

Sodium silicate according to the invention is preferably in amount of 0.5 - 20%, preferably 1 - 15%, based on the weight of activated clay. Smaller amounts may demonstrate no effect, while greater amounts may hinder color formation.

A dispersant co-used with sodium silicate is preferably in an amount of 0.1 - 15%, preferably 1 - 8%, based on the weight of activated clay. Smaller amounts may demonstrate no effect, while greater amounts do not adversely affect the viscosity but may reduce color-forming capabilities. Particularly eligible dispersants used in combination with sodium silicate include sodium pyrophosphate, sodium tri-polyphosphate and sodium hexametaphosphate.

Activated clay together with the above dispersants is dispersed in water and with known pigments,

adhesive compounds and additives forms a coating liquid to

be applied onto a substrate such as paper. A particularly suitable pigment is calcium carbonate. As an eligible adhesive, there may be used polyvinyl alcohol and styrene-butadiene latexes.

Since activated clay particles are amorphous, and porous, they require more adhesives than do other paper making clays such as kaolin, calcium carbonate and the like in order to obtain a sufficient strength of the coated layer for printing. However, attempts to use added amounts of synthetic rubber latexes, starch, casein, CMC and other water-soluble adhesive compounds as commonly used in art papers and coated papers would result in blocked activation of the activated clay and hence in reduced color-forming capabilities.

Whereas, the sodium silicate according to the invention serves satisfactorily as a dispersant for the amorphous, porous activated clay and as a water-soluble inorganic adhesive as well, without hindering color formation unlike conventional synthetic rubber latexes and naturally occurring organic water-soluble adhesive compounds. Rather it

acts to enhance color-developing ability of the activated clay. Consequently, the use of the sodium silicate^{can} lead to saving of the adhesive compounds.

Oxides, hydroxides and carbonates of alkali or alkali earth metal are known to enhance the ability of activated clay as disclosed for example in Japanese Patent Publications No. 41-2373 and No. 42-8811. However, either addition of activated clay after sodium silicate has been first added to water, or addition of sodium silicate after activated clay

has been first dispersed in water would result in a system which gelled as a whole.

A satisfactorily fluid, high-concentration coating liquid can be obtained according to the invention by using an activated clay in a particulate solid form which has been in advance admixed with sodium silicate and optionally other dispersants. Such coating liquid may be conveniently applied by a blade coater to a substrate to produce a color-developer sheet which has a good surface quality free from smudge on contact with encapsulated surfaces and which is sufficiently strong and further free from blanket smear, picking and other troubles which would otherwise occur during printing. These advantages are obtained particularly with use of a blade coater, but may be retained even with an air-knife coater provided that the coating liquid is somewhat reduced in concentration.

The invention will be further described by way of the following examples wherein a commercially available "Mitsubishi-NIC Upper-Sheet 40" was used as the color-former sheet.

Example 1

105 wt. parts of activated clay obtained by dry mixing 5 wt. parts of No.1 sodium silicate (general formula $\text{Na}_2\text{O} \cdot 0.2\text{SiO}_2$, manufactured by Asahi Denka Co., Ltd.) with 100 wt. parts activated clay both in the powder state, is gently added to a solution obtained by mixing 50 wt. parts of 10% polyvinyl alcohol (PVA-105, manufactured by Kurare Co., Ltd., saponification degree 98.5 mol %, polymerization degree 500) with 60 wt. parts of added water, and well dispersed in it. 10 wt. parts (solids content) of styrene butadiene latex (Dow 670, styrene about 60 wt.% are added and well stirred and the pH is adjusted to 9.5 with 20% caustic soda. The resulting coating liquid is coated on quality paper 40 g/m^2 by means of a blade coater to give a 8 g/m^2 (solids content) coating.

Example 2

No.1 sodium silicate as shown in Example 1 is replaced by No.3 sodium silicate in equivalent amount (general formula $\text{Na}_2\text{O} \cdot 0.3 \text{SiO}_2$).

Comparison Example 1

After 3 wt. parts of sodium pyrophosphate is added into 60 wt. parts of added water and thoroughly dissolved, 100 wt. parts of activated clay is gently added. 50 wt. parts of 10%, polyvinyl alcohol (PVA-105) aqueous solution is added and well dispersed and 10 wt. parts (solids content) of styrene butadiene latex (Dow 670), and the pH adjusted to 9.5 with 20% caustic soda. The resulting coating liquid is coated on quality paper of 40 g/m^2 by means of a blade coater so that the coating amount is 8 g/m^2 (solids content).

Comparison Example 2

100 wt. parts of activated clay dry mixed with 3 wt. parts of sodium pyrophosphate in powder state is added with stirring to a solution obtained by mixing 50 wt. parts of aqueous solution of 10% polyvinyl alcohol (PVA-105) with 60 wt. parts of added water. 10 wt. parts (solids content) of styrene-butadiene latex (Dow 670) is added and well stirred and the pH is adjusted to 9.5 with 20% caustic soda. The coating liquid so prepared is coated on quality paper of 40 g/m^2 by means of a blade coater to give an 8 g/m^2 (solids content) coating.

Comparison Example 3

5 wt. parts of No.1 sodium silicate in powder state and 100 wt. parts of activated clay in powder state are mixed with 50 wt. parts of 10% polyvinyl alcohol (PVA-105) aqueous solution and 60 wt. parts of added water. With stirring, 10 wt. parts (solids content) of styrene butadiene latex (Dow 607) are added and well stirred and the pH is adjusted to 9.5 with 20% caustic soda. The resulting coating liquid is coated on quality paper of 40 g/m^2 by means of a blade coater to give an 8 g/m^2 (solids content) coating.

Comparison Example 4

100 wt. parts of activated clay in powder state and 3 wt. parts of sodium pyrophosphate in powder state are mixed with a solution obtained by mixing 10 wt. parts of 50% No.1 sodium silicate aqueous solution with 50 wt. parts of 10% polyvinyl alcohol (PVA-105) aqueous solution. The suspension is gently mixed with 60 wt. parts of water with stirring and

then with 10 wt. parts (solids content) of styrene-butadiene latex (Dow 607). The pH is adjusted to 9.5 with 20% caustic soda and the coating liquid thus prepared. This coating liquid is coated on quality paper of 40 g/m^2 by means of blade coater so that the coating amount may indicate 8 g/m^2 (solids content).

Testing Procedures

The coating liquids and the sheets coated therewith were tested as follows:

(1) Coating Liquids

(i) Viscosity

Rotor No. 4 equipped with B-type Viscosimeter (Tokyo Instruments K.K.) was used to determine the c.p.s. value at 60 r.p.m. after a lapse of 1 minute. Hercules II High-Shear Viscosimeter (Nippon Rigaku Kogyo K.K.) was used to obtain the viscosity curves.

(ii) Solid Content.

Determined by drying at 110°C for 16 hours.

(2) Color-Developer Sheets

(i) Smoothness

Tested by Beck Smoothness Tester (Kumagaya Riki K.K.). The greater numerical values mean better smoothness.

(ii) Smudge Resistance

The color-developer sheets brought into rubbed contact with the aforementioned color-former sheet at 300 g/cm^2 , and the smudge generated thereby was determined for its reflectance (%) measured by color Differentiometer (Nippon Denshoku).

The greater numerical values mean less smudge.

(iii) Surface Strength

Tested by IGT tester (Kumagaya Riki K.K.) using IPI No. 4 Ink and B-spring, with the results indicated by the marks  and . The mark  is used to mean "Good".

The mark  means "Fair".

(iv) Blanket Smear (Piling)

Miyaster Type-17 Printing Machine (Miyakoshi Kikai K.K.) was used to make this test with a commercially available off-set ink (blue). The results were indicated by the marks  and X. The mark X means "Bad".

(v) Color-forming Concentration

The color-developer sheets were each combined with the aforementioned color-former sheet and passed over a calender at 96 kg/cm^2 and the color generated thereby was determined for its concentration by the formula

$$\text{Color Concentration}(\%) = \frac{\text{Reflectance of colored area}}{\text{Reflectance of uncolored area}} \times 100$$

wherein the reflectance was measured by Color-Differentiometer (Nippon Denshoku) one hour after passage over the calender.

Test Results

Table 1 (Coating Liquids)

	Viscosity (cps)	Solid (%)	Fluidity
Example 1	1,000	49.2	Good
Example 2	1,210	49.6	Good
Comparative Example 1	4,500	49.4	Highly viscous
Comparative Example 2	2,830	49.6	Gelled
Comparative Example 3	3,050	49.6	Gelled
Comparative Example 4	6,300	49.5	Highly viscous

The above tabulated data are demonstrative of the fact that the coating liquids of examples 1 and 2 according to the invention contain about the same solids as but far excel those of Comparative Examples 1, 2, 3 and 4 in the physical qualities.

Table 2 (Color-developer Sheets)

	Smoothness (sec)	Smudge Resistance	Surface Strength	Color Concentration	Blanket Smear
Example 1	92	90.8	○	24.7	○
Example 2	95	91.1	○	25.2	○
Comparative Example 1	53	87.2	△	24.2	×
Comparative Example 2	68	86.8	△	25.2	×
Comparative Example 3	62	86.2	△	24.6	×
Comparative Example 4	49	85.7	△	25.5	×

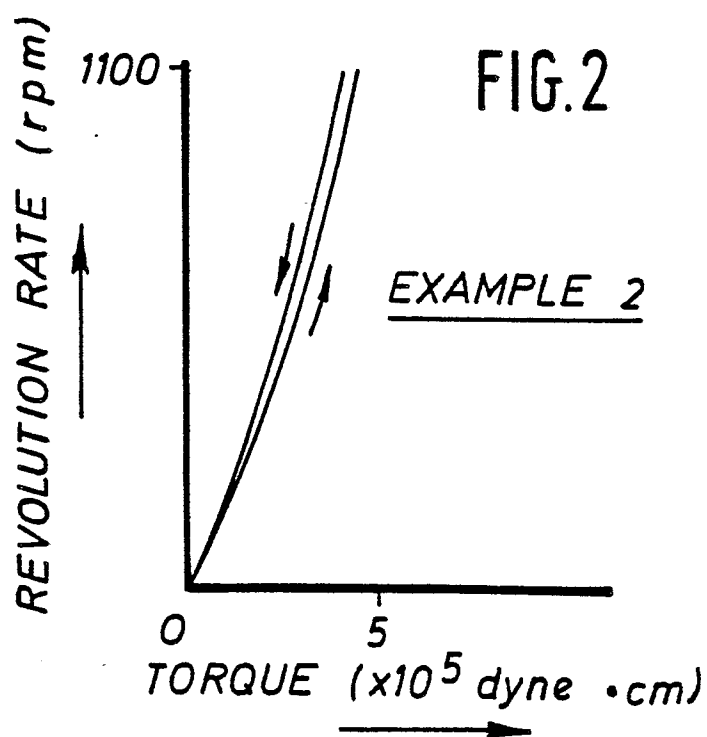
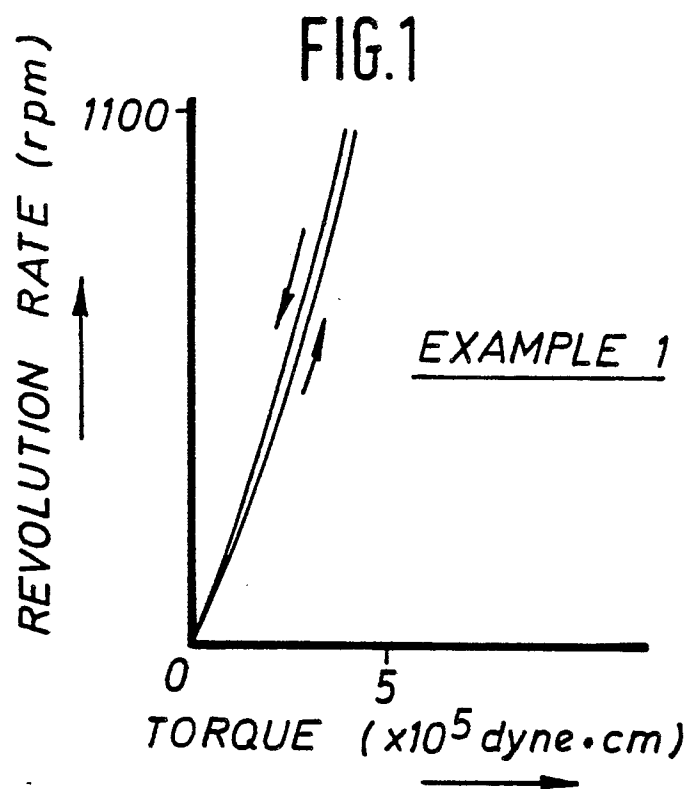
The above tabulated data are demonstrative of the fact that the use of activated clay in particulate form which has been in advance admixed with sodium silicate and other dispersants is effective in imparting satisfactory viscosity to a coating liquid as well as enhanced physical qualities to a color-developer sheet.

4. Brief Description of the Drawings

FIGS. 1 and 2 each are a rheological graph representing Examples 1 and 2; and FIGS. 3 - 6 each are a rheological graph representing Comparative Examples 1 - 4, respectively.

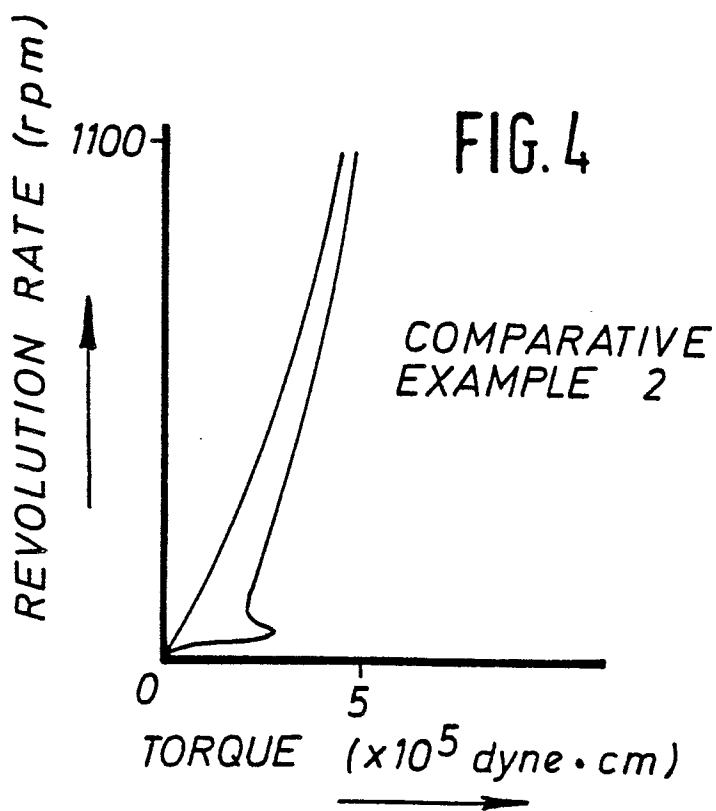
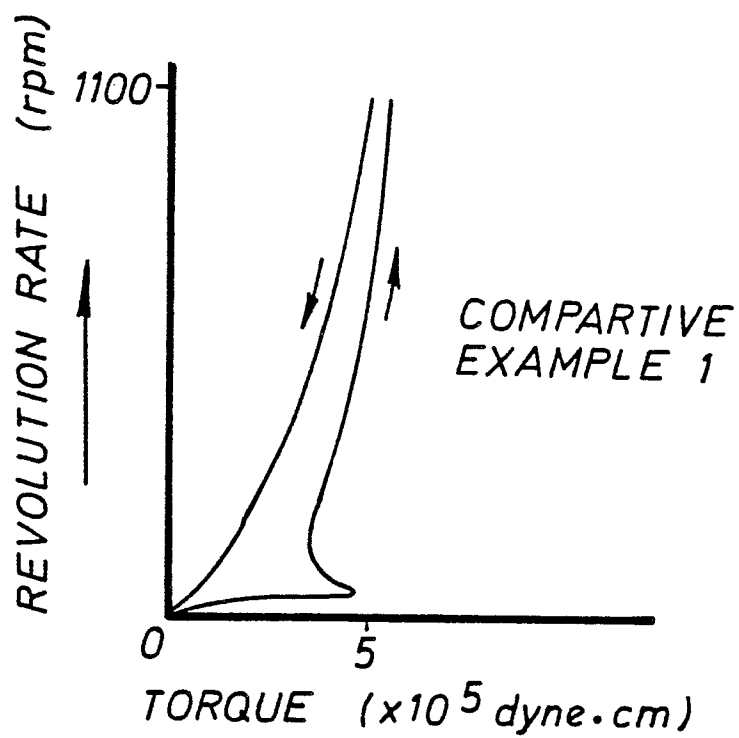
CLAIMS:

1. A color-developer sheet or set for carbonless copying comprising, in combination, microcapsules containing an electron-donative, colorless organic compound and an activated clay capable of developing a color upon absorption of said organic compound, characterised in that a coating liquid is used comprising an activated clay in solid particulate form which has been admixed in advance with sodium silicate and optionally one or more other dispersants.
2. A color-developer sheet or set according to claim 1 wherein said sodium silicate is used in an amount of 0.5 - 20% based on the weight of said activated clay.
3. A color-developer sheet according to claim 2 wherein said amount is 1 - 15%.
4. A color-developer sheet or set according to any preceding claim wherein said other dispersants are used in an amount of 0.1 - 15% based on the weight of said activated clay.
5. A color-developer sheet or set according to claim 4 wherein said amount is 1 - 8%.
6. A color-developer sheet or set according to any preceding claim wherein said other dispersant is sodium pyrophosphate and/or sodium tripolyphosphate and/or sodium hexametaphosphate.
7. A color-developer sheet or set according to any preceding claim made by use of a coating liquid 45% or greater in concentration (solids by weight).



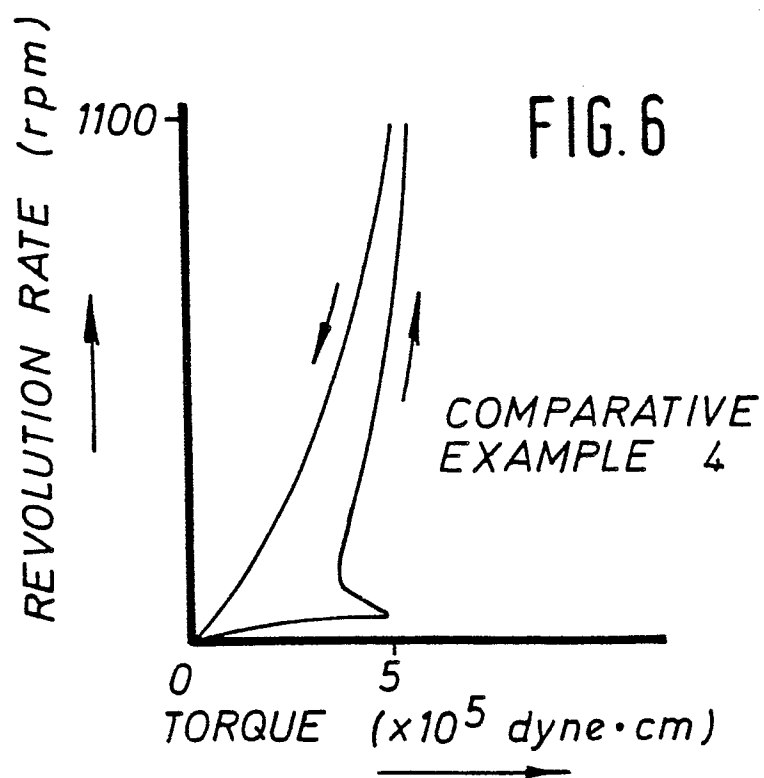
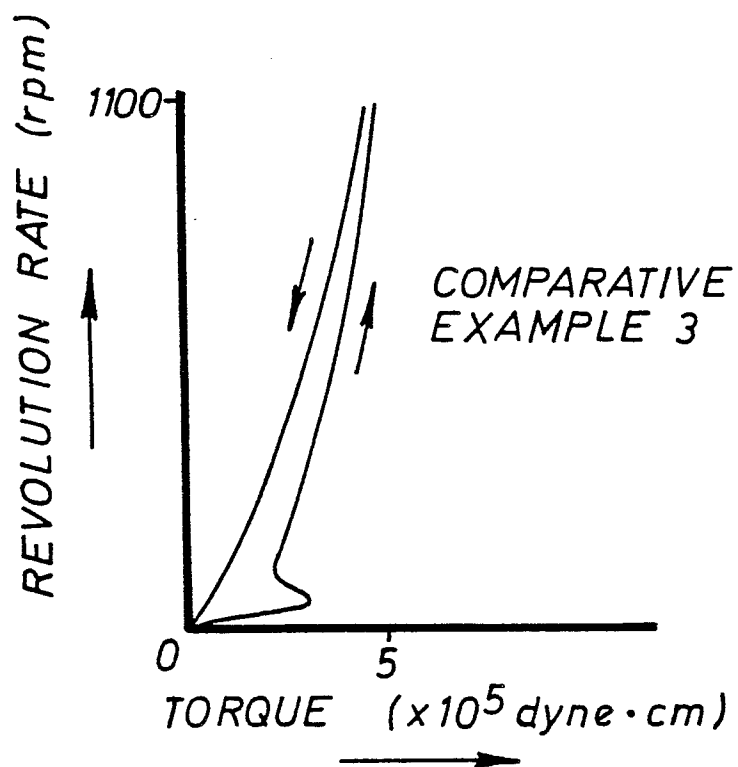
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FIG. 3



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FIG. 5





European Patent
Office

EUROPEAN SEARCH REPORT

0076342

Application number

EP 81 30 4550

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	GB - A - 2 050 407 (MITSUBISHI PAPER MILLS) * Claims; page 1, line 84 - page 2, line 8 *	1-7	B 41 M 5/12
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X	DE - B - 1 152 429 (NCR) * Claims *	1-7	
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X	US - A - 3 223 546 (G.A. HEMSTOCK) * Column 6, line 65; column 7, line 16 *	1-7	TECHNICAL FIELDS SEARCHED (Int Cl. 3)
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A	US - A - 3 434 864 (W.L. HADEN et al.) * Column 7, lines 1-4 *	1-7	B 41 M 5/00
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A	DE - C - 1 001 292 (NCR) * Claims * & GB - A - 760 080	1-7	

			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons
			& member of the same patent family, corresponding document
X	The present search report has been drawn up for all claims		
Place of search The Hague		Date of completion of the search 27-04-1982	Examiner RASSCHAERT