



## Inks for printing on plastic films.

### Composition of polyurethane inks for rotogravure and flexography.

Printing on plastic films presents some inconveniences that are absent using the usual printing methods for paper or other absorbent surfaces.

It's necessary to formulate products able to obtain satisfactory adhesion between the ink and the impenetrable smooth surfaces. In some cases, films such as polyolephines have to be pre-treated because of their inertness. On the other hand, an extra adhesion on the support could give rise to swelling, loss of mechanical properties or too much stickiness.

Ink must have **adhesion** and **cohesion** properties. Moreover, it's often required that it is flexible, glossy, fast to dry, resistant to heat-sealing and, most of all, that it doesn't contain chemicals able to migrate through the film and alter the content of the packaging.

According to different employments, the a.m. requirements have different relevance. For instance, to the inks for internal printing a good affinity with the adhesive used is required but glossy is negligible.

Composition of inks for printing on plastic films, change according to the printing method used.

The **solid**<sup>1</sup> content of rotogravure inks indicatively varies from the 21 to the 54%, that of the flexography from 22 to 59%. At the same time as the rotogravure printing involves the direct inking of the roller that runs on the film, in flexography the ink is transferred on

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<sup>1</sup> The solid content or dry content is the part of solid substances present in the dispersion expressed as percentage.

the film surface after some steps. This fact implies the need of a higher solid content in flexography than in rotogravure.

Another basic difference between rotogravure and flexography inks is related to the **solvent-systems** usable for the two printing methods. The choice of the solvent system primarily depends on their intrinsic properties, as the capability of dissolving the resins and the drying time. The quality of the printed matter is connected to the quantity of residual solvent on the printed surface. On non-absorbing materials the drying of the ink produces a uniform film: that's why the ink has to have a good rheology. Problems can be avoided by an accurate formulation of the ink.

Further, must be considered the laws as concerns the emission of solvents in the atmosphere. In Italy laws regarding the recovery of solvents, force to produce rotogravure inks only with a mono-solvent system. It is necessary for it to use a solvent system, which can allow the recovering. It is normally used only ethyl acetate (recovered at the end of the printing process with suitable recovering plants)<sup>2</sup> sometimes with the addition of small quantities (4-8% max) of ethyl alcohol or isopropyl alcohol when is necessary to *slow down* the ink<sup>3</sup>. In flexography is used a lower printing speed with respect to rotogravure printing and it is necessary to leave the *film opened* for a longer time making easy the homogeneous evaporation of the solvent to allow the film distension. Thus, in flexography there is a tendency to use a bi-solvent system. If the printing is made with a rubber plate resistant to esters<sup>4</sup>, a good solution is to use ethyl acetate and ethyl alcohol (solvent with a slower evaporation)<sup>5</sup> in a mixture (30:70 or 20:80)<sup>6</sup>.

SINTOCHEM offer always mono-solvent products to try to meet the needs of its customers regarding the solvent recovery.

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<sup>2</sup> One recovering method is based on filtration on activated carbon and subsequent extraction with steam or nitrogen gas. Alternatively, small productive realities choose catalytic combustion. The ethyl acetate recovered in these ways, after bi-distillation, usually contain the 0,05-0,07% of water and, if suitably pure, could be used in following stages of the converting process (as for dilution of polyurethane adhesives and inks).

<sup>3</sup> In the same way can be used other retarders in the solvent mixture like methoxy propanol.

<sup>4</sup> In flexography generally the printing roll is covered with acrylic copolymers, which are well resistant to alcohols but only to a limited degree to esters. The last are commonly included in the formulations being excellent solvents for the nitrocellulose.

<sup>5</sup> Among other things, it's important to have an efficacious drying of the solvent because of international regulations limit the esters' concentrations in printed articles to be used in food packaging.

<sup>6</sup> Spanish ink producers and converters frequently use the 20:80 mixture.

Regulations limiting the solvent emissions in the atmosphere, force ink producers and converters to analyse the possibility of using only **water based inks** or mixtures of water and alcohols.

Unfortunately, the printing speeds reached in the production of the flexible packaging whether by rotogravure method (round about 200-300 m/min) or by flexography (almost 100-150 m/min), make hard to consider of using slowly evaporating solvents like water.

To dry the printed surfaces in a reasonably short time it should be necessary to use high temperatures, that are incompatible with plastic films which are sensible to heating. Thus, the development of water based inks interests first off all the printing on absorbent materials, and in few cases mixtures of water and alcohols are used in flexography, but the use of water based inks in high speed rotogravure have to be excluded.

Components	Indicative composition (p.p.)	
	Rotogravure	Flexography
Pigments	6-30	6,5-35
Nitrocellulose	7-10	7-10
Plasticizers	1-3	1-3
Polyurethanic Resins <sup>‡</sup>	7-10	7-10
Ketonic Resins*	1-3	1-3
Solid content	21-54	22-59
Solvents	46-79	41-78

<sup>‡</sup> Resins 80% solid content in E.A.

\* Used only for a high glossy degree, not for laminations.

According to the following table there is a big difference between the amounts that have to be added to obtain white inks and coloured ones.

Pigments	Indicative composition (p.p.)	
	Rotogravure	Flexography
White pigment (TiO <sub>2</sub> )	25-30	27-35
Coloured pigment	6-9	6,5-15

The amount of pigments introduced in the inks formulation depends on various factors such as its transparency, intensity, tone, and affinity with the vehicle. Among the others, have to be considered that some characteristics of the pigments, such as viscosity and solubility, affect the final product characteristics; for example the yellow pigments that have a particularly high viscosity cannot be introduced in formulation in quantity higher than 6-6,5% without endangering the product quality.

- Indicative content of white pigment (TiO<sub>2</sub>): 25-30%
- Indicative content of coloured pigments (basically organic pigments): from 6% to 9% for rotogravure printing method and from 6,5-7% to 12-15% for flexography.

It could be sometimes necessary to add organic salts to help the titanium oxide dispersion and, in the same time, to obtain advantages related to colour homogeny and gloss of the printed film.

**Nitrocellulose**<sup>7</sup> (plasticized or not) is one of the basic substances for ink formulations, whether mono- than bi-components<sup>8</sup> (of which constitutes the 7-10%). It is a largely used material because of it is easy to dry, economic, film-forming, heat-resistant, soluble in alcohol-ethers mixtures, esters, ketones and dilutable in hydrocarbons. It has low odour, a good degree of dimensional stability and a limited resistance to acids and alkalis.

The stiffness of nitrocellulose implies the addition of plasticizers in the ink formulation (1-3% content).

The plasticizers could be classified in:

- Primary or jellying:  
They are generally chemical compounds with a good polarity able to solve the nitrocellulose. Phthalates were largely used in past but nowadays their use is not permitted according to the international regulations. In consequence, currently most used are citrates and adipates. Excess could cause loss of heat-resistance and adhesion.
  
- Secondary or not jellying:  
They are compounds with low polarity, generally oils with extended aliphatic chains, for ex. stearic esters.

Habitually, an expert formulator is used to optimise his product balancing primary and secondary plasticizers in order to obtain the required effect.

Plasticizers confer a high degree of gloss, a better fixing to the supports and, most of all, they grant the *solvent release*.

As a matter of fact, some of them cause a peptising effect reducing the micellar size and favouring the solvent release. Moreover, the micellar size reduction in the ink confers a high degree of gloss to the printed matter. A similar effect could be obtained reducing the size of the pigment particles in solution to get a system in which the dyes are fully soluble.

Furthermore, the gloss degree could be enhanced adding small percentages (2-3%) of ketonic resins.

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<sup>7</sup> Other commonly used resins are: ethyl-cellulose, polyamide, acrylic, vinylic, maleic.

<sup>8</sup> Mono-component paints and inks are nitrocellulose based thermoplastic products; the bi-components are more heat-resistant with respect to the mono- and are produced adding a cross-linker (thermoset substance) to the nitrocellulose base.

An important matter in the formulation of inks for plastic films printing is the choice of the binders.

The choice of the appropriate system is taken in order to have the desired balance of the characteristics:

- Good pigment dispersion;
- Possibility of printing on the desired plastic supports;
- Possibility of lamination of the printed materials;
- Rapidity of the solvent release with the smallest amount of solvent kept by the ink;
- Good solubility in the solvent system preferred.

Useful binders for the ink formulations are the **polyurethane resins** (7-10%). They are thermoplastic resins that confer flexibility, elasticity, a good thermo resistance (particularly polyurethanes with high and medium molecular weights)<sup>9</sup> and, most of all, an excellent fixing to the plastic film.

Using **catalysts**, such as the titanium acetyl acetonate could be realized products with an excellent fixing degree<sup>10,11</sup>.

Polyurethane with low molecular weight and low viscosity can be utilized as plastifiers; the high molecular weight ones could present a higher stiffness and a higher solvent retention, but their use could be appropriate when is necessary to improve the adhesion and to reduce the migration tendency through the plastic film.

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<sup>9</sup> Regarding the thermo resistance:

A nitrocellulose-based ink added with titanium oxide and polyurethane could resist at 120-130°C for 1 or 2 seconds. Using a suitable cross linker catalyst, the resistance goes to 180°C after 24-48 hours. This effect is due to the improved cross-linking.

For similar reasons a further increasing in the thermo resistance could be obtained using in the ink formulation a higher percentage of nitrocellulose and a reduced amount of polyurethane (plasticising), which could be substituted by a monomeric plasticizer. In the last case is better to add a small quantity (1-2%) of ethylcellulose to avoid a likely yellowing of the product due to the high quantity of nitrocellulose.

<sup>10</sup> At molecular level, the printing process involves the formation of a "bridge" constituted by a titanium atom attached between the plastic film and the ink. Actually the heating effect causes the shift of the ligands originally bounded to the titanium (for example: acetyl acetonate or phosphate groups) and the following coordination by the polyurethane ligands and the oxygen atoms, active for the coordination, that are on the surface of the printing support. Between the two coordination complexes above mentioned it could be noticed that the shift of phosphates is slower than the others, being its molecular weight higher.

<sup>11</sup> To improve the adhesion property it could be increased the amount of catalyst titanium based or could be added alcoholate compounds like butyl- or isopropyl- titanate. Alternatively it could be reduced the pigment content (but only if it is compatible with the covering required).

Low gloss degree and opacity generally characterize polyurethane inks.

The gloss degree could be enhanced with an accurate balancing of the **ketonic resins** content in the formulation<sup>12</sup>.

A higher gloss degree could be obtained adding a small quantity of **maleic resins** too. The last are also used to improve the thickness and to reduce the tixotropy<sup>13,14</sup>.

Higher gloss degree inks can be obtained using **polyamide** resins. They confer good resistances and printability too. On the other hand they could presents undesired effects such as unpleasant odour and **tixotropy** and aren't suitable for laminated or high temperature applications.

Glossy inks, with high thermo-resistance and resistance to scratch could be prepared also using a combination of **acrylic** and **polyester** resins together with isocyanate hardener.

Acrylic resins have good adhesion on PVDC coated films and are used in the water-based ink formulations.

Nitro-urethane based products don't have a high **resistance to the light**; in fact, nitrocellulose and aromatic urethanes are easy to turn to yellow<sup>15</sup>. Yellowing is avoided in case of aliphatic polyurethanes are used. They are also generally characterized by a superior plasticity and a lower cohesion degree than the analogue aromatic compounds.

Ink formulations frequently include the presence of **stabilizers** that help to cut the oxidation.

In past was commonly used the BHT ( $\beta$ -hydroxyl toluene). Unfortunately, reacting with the oxygen it give rise a yellow ketone compound characterized by a high migration.

Alternatively could be used stabilizers constituted by molecules with a greater size, formed by two or more aromatic rings, that have a lower tendency to migrate and are more effective too (for example: Irganox-CIBA).

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<sup>12</sup> Furthermore adding ketone compounds enhance the polyurethane solubility.

<sup>13</sup> Maleic resins are slightly acid and hygroscopicity.

<sup>14</sup> Tixotropy is the tendency of a pasty substance to liquefy when shaken and to become solid (gel) again when keeps still.

<sup>15</sup> To avoid the yellowing of products with a high percentage of nitrocellulose, it is possible to substitute a small part of it with ethylcellulose.

Other kinds of ink formulations are based on different binders than polyurethane. Systems based on **maleic, acrylic, ketonic, polyamide, polyvinyl (PVB) resins** are commonly used. The last are particularly thermo resistant and glossy. Maleic or fumaric resins (acidic) based systems are characterized by excellent fixing and glossy but have a low softening point and high hygroscopicity. Acrylic and ketone resins confer a high gloss degree and fixing too, but low thermo resistance and solvent retention.