

Customer Guidance

Guidance for the Safe Use of Cellulose Nitrate Printing Inks and Related Products

1. Introduction

This document sets out some guidance for the safe use and handling of printing inks and related products that contain cellulose nitrate (commonly called nitrocellulose or NC).

Printing inks (and related products) based on nitrocellulose represent a very common and versatile solvent ink type in rotogravure and flexographic printing of packaging's. Nitrocellulose, as a basic binder polymer, is essential for a number of required properties in packaging (pigment wetting, heat-seal resistance, solvent release, brilliance, etc.).

2. Hazardous Properties of Cellulose Nitrate

Differing from other flammable or combustible materials, substances with nitro groups like cellulose nitrate are able to decompose violently without needing airborne oxygen, producing, among other reaction products, toxic nitrous gases. Consequently, cellulose nitrate grades and other nitro compounds with high nitrogen content belong to the category of explosives.

However, such grades are never used as components of inks and related products. NC inks are always based on solutions of cellulose nitrate with a low degree of nitration, and consequently they are less dangerous.

In addition, any associated risk is minor since cellulose nitrate normally accounts for less than 20 % of the product, remains wetted/damped in normal storage and use, and is combined with other binders and/or additives, which act as desensitizing agents.

The user should however **be aware of some potential risks** associated with the handling of NC-containing inks, in particular regarding waste ink storage and collection and cleaning solvent distillation, which require additional controls to those necessary for risk management practices of solvent borne systems that do not contain NC. These potential risks are:

- **exothermic reaction** (generating heat and fumes) and/or self-ignition particularly in the **presence of other components capable of causing catalytic decomposition** of cellulose nitrate: examples are **aluminium, transition metals, copper or brass, acids or acidic resins, amines/aminoalcohols or amino-resins, oxidizing agents**, etc.
- flammability or self-ignition if **concentrated** and/or **dry**
- self-ignition at **temperature in excess of 140°C**

The effects may vary from simple release of fumes containing toxic nitrous gases (reddish or brownish, typically), to induction of a fire and vapour explosion. Decomposition may remain unobserved for some time due to slow smouldering. As a rule, the higher the concentration of cellulose nitrate, the higher the temperature and the more substances able to react with it that are present, the higher is the risk of self-ignition. Note also that the decomposition of NC is an exothermic reaction causing continually increasing temperature (and possibly pressure) in an insulated (also called an adiabatic or isocaloric) environment. This could be highly dangerous in a confined space such as a distillation unit.

3. Safety Management: User's Responsibility

Industrial safety legislation concerning the control of hazardous products makes the **user fully responsible for ensuring the safe application and use of the ink**, including the treatment of by-products and the disposal of waste. The responsibility of the ink supplier is focused to ensure transmission of product or product group related Safety Data Sheets containing sufficient and relevant information for the user to carry out his responsibilities.

To support the quality of users' safety management in accordance with applicable regulations, EuPIA Technical Committee - committed to Responsible Care®/Coatings Care® principles - has drawn up the following detailed information on specific risks connected with NC inks and related advice for safety measures.

3.1 Waste Collection

Exothermic reactions may occur if NC inks come into contact with other ink types or other chemicals used in the printing processes that contain substances that may react in a hazardous manner with cellulose nitrate, e.g.:

- Water based inks containing ammonia or aminoalcohols
- UV-curing inks and varnishes containing amino-compounds
- Non NC-based solvent inks which contain or may contain alkaline additives
- Special care is recommended when using any ink related products or other printing shop chemicals that may contain acid, alkaline substances or metals in concentrated form.
- Care should be taken to ensure any removal of NC is carried out in line with the Transport of dangerous goods regulations for special waste applicable to the country of operation

Advice for safety measures:

- **Collect, store and dispose of NC-containing waste separately from other ink types** and other chemical products
- Store NC-containing waste in suitable **safety containers** in a safe place **away from production areas**
- **Check your solid waste streams for occurrence of critical residues** (that is, mixtures of NC-containing residues with residues containing substances that could react with NC); establish, where appropriate, separate collection and controlled disposal.
- **Avoid friction, rub or other mechanical treatments for waste residuals/crusts/encrustations.**
- Consult ink manufacturers advice related to the particular product risks and measures.

3.2 Dry-out of NC containing mixtures (not phlegmatized)

Dry or nearly dry spilled layers or significant residues of NC-containing products may self-ignite. Dry or nearly dry NC is readily combustible, so any fire will propagate rapidly. Striking or dropping objects onto dried NC products can cause ignition.

Advice for safety measures:

- **Clean** splashes or spills from floors, walls, drains or (hidden) equipment parts with cleaning water **as soon as they occur**. Do not allow them to dry out.
- Do not remove dried residues by scraping. In case of need, use non sparking tools, like brass or stainless steel, operating in wet conditions, using water.
- Do not let residual portions of NC ink, ink mixtures and wastes in containers dry out. Always **close containers securely**.
- Storage of waste drums containing NC deposits or empty NC solution waste should not be stored in direct sunlight, or below radiated sunlight which may heat the product
- **Never dispose of** dry or liquid NC containing products **in waste/rubbish bins**. Use appropriate safety tins with closure.

- **Apply appropriate controls to the storage of cleaning rags (“wipers”) that are contaminated with NC containing ink or related material.** Particular care is required if rags contain concentrated amounts of NC such as those that may be present following the cleaning-up of a spill. Other used/contaminated spill control materials also need to be stored appropriately.

3.3 Distillation

Many printers process and generate used **cleaning solvents** and **ink residues** in-house. Either batch or continuous distillation processes are employed.

Indications given in this guidance are not intended to free printers from their responsibilities but are meant to contribute to improving the knowledge on existing prescriptions and their implementation. In any case, printers should carefully consider the recommendations made by the distillation equipment manufacturers.

Before starting any distillation, please advise your distillation equipment supplier that you intend to operate with nitrocellulose containing materials.

As basic information, the following hazardous conditions, capable of triggering exothermic reactions and consequently solvent vapour explosions, may occur:

- Evaporation of distillation residues due to dryness, e.g. by absence of monitoring or if switch-off is effected by pre-set time only.
- Presence of aluminium or brass pigments, acid and/or alkaline components in combination and in high concentrations.
- Product temperatures higher than 100°C.
- Locally overheated zones when vessel content remains unmixed (“hot spots”).
- Material enrichment, decomposition and overheating in encrustations.
- Friction of the stirrer with container’s walls, if dry or low level conditions are present. Also problems in alignment of the stirrer have to be taken in consideration.

Advice for safety measures:

3.3.1. Suitability and equipment of the distillation unit:

- **Specify and check suitability** of new or existing distillation equipment for processing NC containing waste - in particular, if secondary exothermic reactants as mentioned above are present seek the advice of **your supplier** (of printing inks or of the equipment).
- Special attention should be paid to checking **for which solids content the distillation unit is appropriate**. Hazards associated with low viscosity liquids with low solids content such as **cleaning solvents** are minor compared to those of pasty, high solids **ink waste**.
- The **product temperature** must be kept **below 100°C**. As a rule, only vacuum distillation meets this specification. The **heating equipment of the vessel** must be monitored using **safety thermostats**.
- To exclude dangerous enrichment of NC and exothermic runaway, the unit should be equipped as follows:
- A **safety switch-off** is the basic requirement: automatic alarm and heat switch-off above a determined critical temperature, triggered by a **temperature sensor** in the **distillation sludge** or at the **entrance of the condenser**.
- A **second control and switch-off** system ensuring **redundancy**, based on a different chemical-physical property, is strongly recommended, e.g.:
 - presence of at least one inspection glass for regular operator sight controls in combination with easy manual emergency heat switch-off, and/or

- a minimum distillation sludge filling level sensor connected to automatic alarm and heat switch-off below a critical value. A suitable alternative may be weighting cells.
- In addition to the safety switch-off at the determined critical temperature, equipment for **emergency cooling** of the content of the vessel is recommended.
- The **content of the vessel** must be **kept reliably agitated**
 - either through the effect of the boiling process
 - or (preferably) by agitators/scrapers made of spark-proof materials.

3.3.2. Rules for operating the unit:

- Remember the fact that dry inks have properties similar to NC properties and therefore can undergo thermal decomposition
- Observe carefully equipment **supplier's process instructions**.
- Get advice from your local **safety supervision authorities** and observe their regulations and guidance.
- **Train the operating staff** carefully and systematically. Include information on risks related to NC and clear instruction on managing NC-containing wastes.
- **Load and distil separately** ink and/or cleaning solvent **wastes originating from the different ink types** identified as critical for exothermic interactions (as in subchapter 3.2).
- **During the ongoing process, new addition** of product to be distilled has to be either **excluded or carefully regulated** in relation to the unloading rate of the sludge.
- After distillation or at appropriate intervals, the **vessel** must be **inspected** and encrustations eliminated with appropriate solvents. In case of need, only non-sparking tools are allowed.
- Do **not fill** containers with distillation residue **when warm**.
- Fill and store residues in suitable safe and firmly **closed containers pre-filled with water away from production** before disposal through an authorized special waste collector.

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Appendix: Examples of National Guidance and Publications

Germany

- Berufsgenossenschaft der chemischen Industrie, Merkblatt M037 (12/93) on "Nitrocellulose" (German); Jedermann-Verlag, Heidelberg
<https://medienshop.bgrci.de/shop/bqi/mreihe?query=/m037.xml&field=path>

UK

- HS017 BCF Guide to storage and Handling of Industrial Nitrocellulose – June 2015 - https://www.coatings.org.uk/Publications/Health_and_Safety_Publications.aspx
- Chemical reaction hazards and the risk of thermal runaway, HSE Books; INDG254 (10/97) <http://www.hse.gov.uk/pubns/indg254.htm>