

A biodegradable, protein-based biopolymer to replace acrylic resins and their additives in textile printing

Abstract

This case story describes an alternative to acrylic resins used in textile printing. The use of acrylic resins is problematic since these are sensitizers and also since they require the use of additional additives that may also be problematic, such as alkyl phenols, phthalates and organotin. Grafcò Srl has developed an alternative polymer based on milk-protein that could replace the acrylic resins along with the required additives.

Substituted substance(s)

1. Methyl methacrylate

CAS No. 80-62-6 **EC No.** 201-297-1 **Index No.** 607-035-00-6

Chemical group Carboxylic acid esters

Classification: R-phrases

R11 Highly flammable

R43 May cause sensitization by skin contact

R37/38 Irritating to respiratory system and skin

Classification: hazard statements

H225 Highly flammable liquid and vapour

H315 Causes skin irritation

H317 May cause an allergic skin reaction

H335 May cause respiratory irritation

Alternative substance(s)

1. Casein acid

Classification

The substance has no harmonised classification according to Annex VI of Regulation (EC)

No 1272/2008 (CLP Regulation)

Application

Sector

Manufacture of textiles, wearing apparel, leather and related products

Function

Agents adsorbing and absorbing gases or liquids

Binding agents

Process

Printing / stamping / flexography / offset / primer

Enterprise using the alternative

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State of Implementation Partial capacity

Availability of alternative(s)

On the market

Producer or supplier

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Reliability of information

Evidence of implementation: there is evidence that the solution was implemented and in use

at time of publication

Hazard assessment

Methyl methacrylate is listed in the "hazardous Substance Database" according to SUBSPORT Screening Criteria (SDSC), since it is classified irritant and sensitizer. Casein acid, which serves as a base of the alternative product has no official hazard classification.

Substitution description

Over the last years the international control bodies have increasingly restricted the hazardous substances broadly used in textile. Consequently, the textile print producers had to develop and implement new chemical formulations.

For many years the Benetton Group has been cooperating with Grafco Srl (Treviso), an industry specialized in the textile pigment printing and committed to the research on sustainable solutions for textile industry. Grafco R&D laboratory has developed a textile printing binder called "PROTEX".

This product is a completely biodegradable milk protein-derived biopolymer, to serve as clear base for textile serigraphy applications. It could replace petrochemical acrylic resins and it is compatible with highly sustainable additives, which can replace those generally used to increase wettability (Alkyl phenols), softness (Phthalates) and time preservation (Organotin compounds) of acrylic resins.

The product is based on protein binders, whose technical features of printability, brightness of colour tones and colourfastness to washing are comparable to the features of the petrochemical derivatives.

The product is compatible to all existing pigments and it is printable on fabric using both screen and rotary printing machines. Grafco R&D laboratory is currently developing a new product version for ink-jet printing.

The disadvantage of this product is the need to store it at low temperature due to its thermo sensitivity: since the product is bio based and biodegradable it can easily be attacked by microorganisms and therefore it should be stored in temperature controlled areas at 10°C or below; this pose a limit to use it for a large scale industrial production. However this problem regards only the storage of the product and not the printing process or the use-phase.

Below is a brief description of the main features that may lead to choose the alternative product as A) Binder-Base; B) wetting agent; C) softener; D) preservative.

A) BINDER-BASE: the acrylic resins are produced by petrochemical substances that are hazardous since they can lead to skin allergic reactions. The alternative product is biodegradable and obtainable from waste substances of dairy industry: it has no known hazards.

B) WETTING AGENT: the acid casein is a natural hydrophilic colloid with sufficient wetting properties. There is an option however to enhance the performance by adding small amounts of 2-Amino-2-methyl-1-propanol, classified environmentally harmful in spite of the additives normally used to this aim, very toxic for aquatic habitat. In fact Alkyl phenols, used in resins-based printing paste, are toxic for reproduction (CMR of category 2) and very dangerous for aquatic environment; they have been long restricted for specific uses and recently they have been included in the list of SVHC substances (Reg. REACH, in "Candidate List" since 19/12/2012).

C) SOFTENER: The softness of the alternative product may be further improved by adding Lanolin. Lanolin is a natural wax drawn from the initial treatment of wool fibers. It is broadly used in cosmetics, thanks to its specific moisturizing and smoothing properties; as a sub-product it is considered to be sustainable. Phthalates are often added to resins-based printing paste to improve their softness and flexibility. Some phthalates are classified as endocrine disruptors, hazardous for human health and aquatic environment and among the first substances subject to Authorization (All. XIV, Reg REACH).

D) PRESERVATIVE: The product is preserved by low temperature storage and acetylsalicylic acid can be added to enhance preservation. Organotin compounds (such as MSDS "DBTC" and "TBTO") are generally used to preserve resin-based printing paste from microorganism attack. These are hazardous to reproduction (CMR, cat.1B) and aquatic life, due to their persistent and bio-accumulative properties (PBT). These compounds, which have long been restricted for specific uses, have been introduced in the "Candidate List" ("Candidate List", Reg. REACH) since December 2012. The performance of a "PROTEX" printed product is comparable to the standard resins-based printing paste: for instance, a dark colour printed on white ground will produce the following:

Colour fastness to domestic and commercial laundering (ISO 105-C06:2010):

Colour change

grade 4-5

| | | |
|--------------------|-------------|-----------|
| Colour staining on | diacetate | grade 4-5 |
| | cotton | grade 4 |
| | nylon 6.6 | grade 4-5 |
| | polyester | grade 4-5 |
| | polyacrylic | grade 4-5 |
| | wool | grade 4-5 |

colour fastness to rubbing

(ISO 105-X12:2001)

| | | |
|-----|-----------|-----------|
| dry | warp/weft | grade 3-4 |
| wet | warp/weft | grade 2-3 |

In summary, the alternative product may not only replace some toxic and polluting substances, but it may also have an additional positive impact on the environment, thanks to its complete biodegradability. In the final life-cycle the "PROTEX" printed products will have a shorter and sustainable decay time compared to products printed with synthesis polymers. In addition, the discharge of printing waste allows for a simple biological purification and may be converted into fertilizer.

Case/substitution evaluation

This case story describes a biodegradable alternative to acrylic resins in textile printing. In addition it also describes how a number of hazardous additives, that are commonly used within acrylic resin printing, can be replaced when using the alternative product. The alternative product has the advantage of being completely biodegradable, this is however also connected to the need to store the product at low temperature. Therefore organisational measures might be undertaken in order to implement this alternative product. Please note that the SUBSPORT team has not evaluated the data on performance of the alternative.

Who provided the information

Type of information supplier

User

Contact

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