



Phthalate-free plasticisers in nitrocellulose (NC) and cellulose acetobutyrate (CAB) systems

Jörg Menrath, Leather Business Unit, LANXESS Deutschland GmbH

Lacquers are formulated to provide the finished leather with the required level of gloss and feel. Nitrocellulose (NC) and, to a lesser extent, cellulose acetobutyrate (CAB) lacquers are widely used. These formulations generally contain plasticisers to give the coatings the required degree of flexibility, and an example is shown in *Panel 1*.

NC-based lacquers are the main type used for garment and shoe upper leathers while CAB systems, because of their superior resistance to yellowing, are preferred for light or pastel coloured furniture upholstery leathers, for example. This is illustrated in *Panel 2*.

Both NC and CAB formulations almost exclusively use combinations of gelatinising and non-gelatinising plasticisers to soften and increase the flexibility of the lacquer films.

Gelatinising plasticisers (which in the past frequently included substances such as phthalic acid dialkyl esters) have the tendency to make the lacquer film - hence the surface of the leather - tacky and “plastic” to touch. This effect can be minimised by adding non-gelatinising plasticisers such as butyl stearate or castor oil. Conversely, gelatinising plasticisers counteract the tendency of the non-gelatinising components to migrate and cause “writing effect” by dissolving them permanently.

While NC and CAB lacquers enhance the natural appearance of the leather, polyurethane (PU) and polyacrylate (PAC) dispersions provide better fastness properties. These are used in the production of shoe upper and furniture leathers, but are especially suited for automotive leathers. Because the flexibility of the lacquer coat can be adjusted by selecting the appropriate monomeric components these systems do not require plasticisers.

Changing regulatory requirements

Since the late 1990s, a number of phthalic acid diesters—in particular those with small alkyl residues of up to 10 carbon atoms, such as di-isodecyl, di-octyl or di-butylphthalate⁽¹⁾—have been significantly re-evaluated, especially where these substances are used in products to which babies and young children might be exposed. Under current EU law^(1,2), a total of six of these phthalates may not be used in toys and baby goods, or only in quantities of less than 0.1 per cent by weight.

Butyl stearate or vegetable oils are generally considered safe, but the phthalates originally used as gelatinising plasticisers required investigation and development.

Although health and ecological issues were paramount, it was most important to develop a plasticiser that could be used for the entire lacquer range, but also to offer a favourable cost benefit ratio. The plasticiser had to be suitable for both solvent-based and waterborne formulations and be compatible with

both low molecular weight, and elastic high molecular weight nitrocelluloses.

Research revealed that adipic acid esters matched this profile best, especially di-(2-ethylhexyl)adipate (DOA). However, the plasticising effect was not always sufficient, particularly in the presence of high molecular weight nitrocelluloses, therefore a second effective plasticising component—dibutyl sebacate (DBS)—was chosen as a co-additive. DBS has a boiling point of 343°C, and a very low volatility, and by varying the mixing ratio of DOA/DBS it is possible to adjust the optimal degree of flexibility for all products and formulations.

The whole NC range has therefore been changed, and it also proved possible to apply this technology directly to the CAB range. This means that binary DOA/DBS plasticiser systems are fully available for both types of lacquer finishes as illustrated in *Panel 3*, also within certain acrylic resin containing CAB based emulsions to optimise the wet rub fastness.

Nitrocellulose and cellulose acetobutyrate lacquers still play an important role in leather finishing and a complete range of products free from alkyl phenols and phthalates is available to meet current and anticipated health and ecological issues. Since these products were introduced - given comparable production and sales volumes - they have provided the same quality and are similar in price to traditional products. This means that ecology and health protection do not have to be more expensive. 🌱

Panel 4: Emulsifiers in waterborne lacquer formulations

From the early 1990s, there have been reservations regarding the ecological effects of alkyl phenols such as nonyl phenol and their ethoxylates. These were widely used in waterborne lacquer formulations and substitution with efficient biodegradable alternatives, such as fatty alcohol ethoxylates has been completed for some time.

Panel 5: Product stewardship in practice

The customer-oriented and transparent approach to the subject of “risk chemicals” is made clear in the Global Restricted Substances List⁽⁴⁾ drawn up by LANXESS for its customers in the leather industry. This list, which is regularly updated, details all the substances which the company no longer uses in the manufacture of leather chemicals either because of legal requirements or as part of the company's voluntary commitment to responsible care. They include numerous phthalates, certain biocides, and persistent organic pollutants such as alkyl phenols and derivatives.



Panel 1: Comparison of the flex resistance of leather samples to flexing—100,000 flexes Bally Flexometer



Nitrocellulose top coat without plasticiser - some defects marked



Cellulose acetobutyrate top coat with plasticiser - no defects marked

Panel 2: Comparison of yellowing resistance



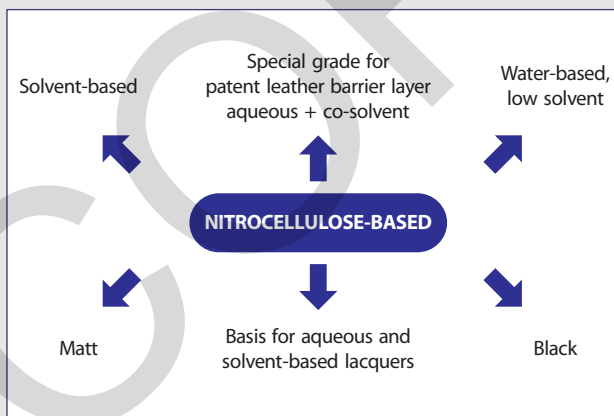
Nitrocellulose lacquer



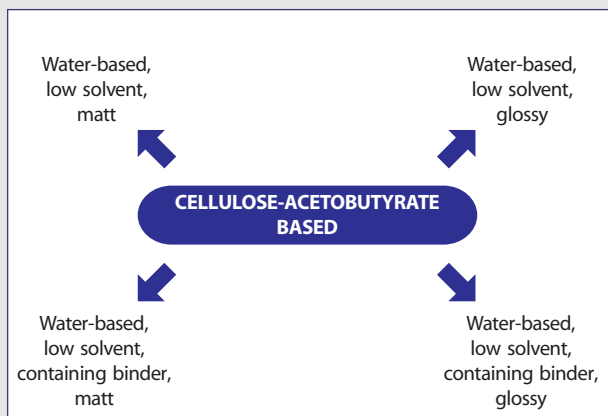
Cellulose acetobutyrate lacquer

NOTE: Inner sample aged 24hr at 120°C
Outer samples not exposed to thermal aging assessment

Panel 3: Phthalate-free plasticisers in lacquers



Nitrocellulose based lacquers



Cellulose acetobutyrate based lacquers

References

1. Decision of the European Commission of December 7, 1999, 1999/815/EC and later extensions;
2. Directive of the European Parliament and Council of December 14, 2005, 2005/84/EC;
3. Directive 2003/53/EC of the European Parliament and Council of June 18, 2003 on the 26th amendment to Directive 76/769/EEC;
4. Lanxess Leather Product Stewardship and Global Restricted Substance List, Lanxess, Leverkusen, February 2010.