



Sustainable leather finishing free of NMP and with reduced VOC

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N-Methylpyrrolidone (NMP) was a popular solvent used in leather finishing for a considerable time. Mainly, it eased the production of binders and the application on leather, hence it was helpful in achieving good performance.

But NMP was found to be reproductive toxic. On June 15, 2001 the state of California added NMP to the list of chemicals known to cause cancer or reproductive toxicity with regard to the so-called Proposition 65.^[1] This was the first toxicological consideration of NMP by law and other restrictions followed.

NMP-free systems were demanded, but there was also a need to reduce the content of volatile organic compounds (VOC) in leather finishes.

Why was NMP used in leather finishing?

Water-based polyurethane binders have excellent properties for leather finishing. Their chemical synthesis is normally made in two steps. In the first reaction a prepolymer with relatively short molecule chains is produced. The problem with this first process step is the strongly rising viscosity as the reaction progresses if undiluted chemicals are used. A dilution

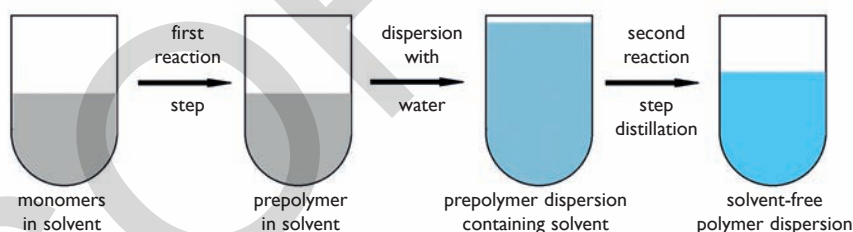
with water is not possible at this stage because of the reactivity of the isocyanates with water. So there are two possibilities that are employed to handle this high viscosity.

- In the so-called acetone process the prepolymer is dissolved in a solvent, mainly acetone, which is distilled off at the end of the polyurethane production. The use of this solvent causes higher costs, as the need for distillation at the end of the process needs more energy and is not of ecological benefit. In addition it requires longer production time and means a loss of reactor capacity.
- In the so-called prepolymer ionomer process, another higher boiling solvent is used in an amount so that the viscosity becomes just manageable. But higher boiling solvents have the disadvantage that they remain in the product. This means that non reactive and non toxic compounds with high flash points are needed: they must also have good solubility properties to polyurethanes and effectively lower the viscosity when used in small amounts. Until NMP was recognised as hazardous it was the ideal solvent.

These two techniques are indicated in *Panel 1*:

Panel 1: Production processes for polyurethane synthesis

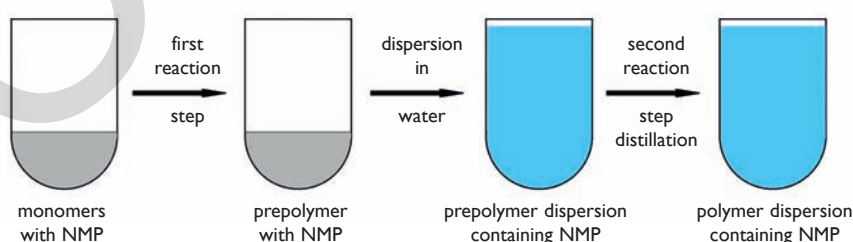
Acetone process



Disadvantages of Acetone process

- ▶ Higher costs
- ▶ Ecologically not beneficial
- ▶ Higher energy consumption
- ▶ Longer production time
- ▶ Less reactor capacity

Prepolymer ionomer process



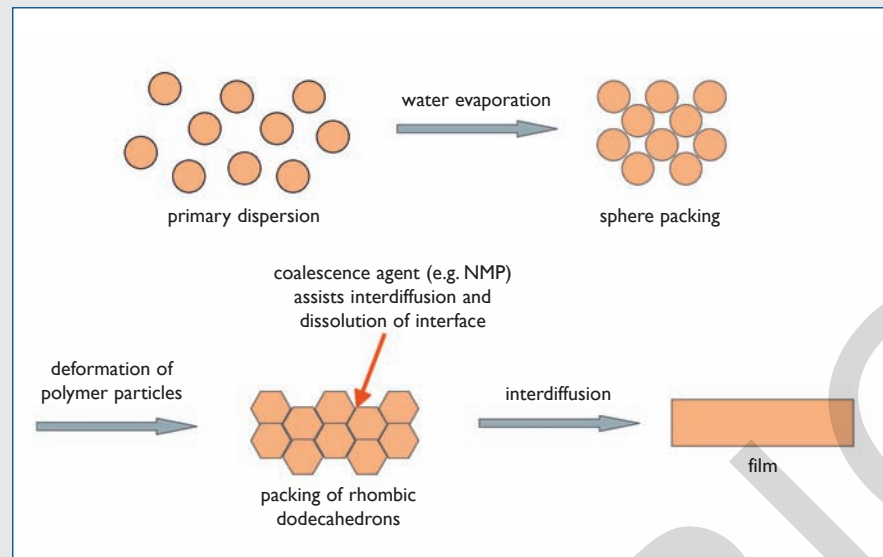
Disadvantages of Prepolymer ionomer process

- ▶ Solvent remains in the product
- ▶ Only few solvents are suitable



In addition, NMP has positive effects on the process of film formation of polymer binders and therefore on many features of the leather coatings, and these are indicated *Panel 2*:

Panel 2: Film formation process

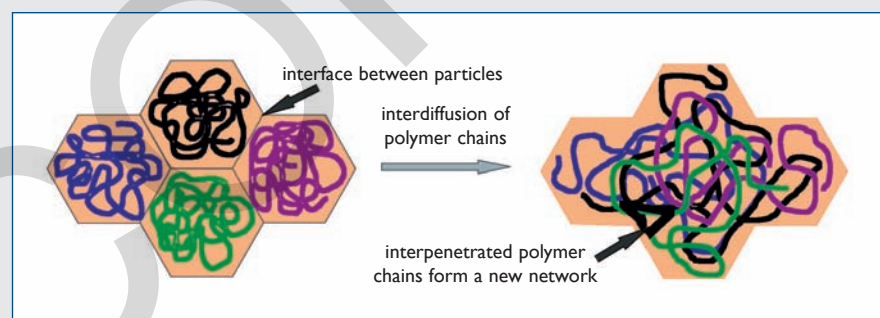


This shows that as aqueous polymer dispersions begin to dry the water evaporates until the dispersion particles form a closed sphere packing. With further evaporation of water the polymer particles begin to deform, and when the water has been removed these particles fill out the complete space with a packing of rhombic dodecahedrons.

But a kind of interface still exists between these particles, and this has to be eliminated within the last film-forming step. In this last process parts of the polymer chains move through their particle interfaces and diffuse into the neighbour particles as indicated in *Panel 3*:

This indicates that bit by bit the polymer chains diffuse into

Panel 3: Interdiffusion of polymer chains



each other and form a new network. This gives the polymer film its mechanical properties such as fastness and elasticity, and this process is supported by coalescence agents such as NMP. These agents remain in the dried film and cause a higher mobility of the polymer chains and a lower surface tension. So the interdiffusion of the polymer chains, and therefore the film formation, becomes easier. This means, for example, that the minimum film forming temperature is lowered by coalescence agents.

In particular, NMP provided other positive effects in leather finishing, especially when the complete system is perhaps a little critical. For example, the levelling can become more even, and a jet blackness can be improved.

NMP: problems in toxicity and VOC

NMP is chemically stable, completely soluble in water, miscible with a broad range of organic substances and neutral in pH. But the new toxicological findings required its elimination within leather finishing, and these pressures were amplified by demands to reduce VOCs. This had to take into account the significant differences in the definition of VOCs in Europe and the USA:

- Europe classifies organic compounds as VOC if their vapour pressure at 20°C or at application temperature respectively is more than 0.1 hPa.^[2] The vapour pressure of NMP at 25°C is 0.4 hPa^[3], so it belongs to VOC regarding to the European definition.
- In the USA VOC are classified as chemical compounds which take part in photochemical reactions in the atmosphere.^[4] So NMP is also classified as VOC in the USA.

The classification as VOC has the aim to reduce the emission and the use of these substances to minimise pollution of the air and environment, and legislators reduce the limits for emissions of such compounds step by step.^[5] To be able to follow these changing limits the use of these substances has to be reduced or investments made into more extensive technology.

The regulations are even more rigorous if toxic or carcinogenic compounds are concerned. In earlier days NMP was thought to be harmless, but new trials showed carcinogenic effects in animals. This new knowledge led the state of California in June 2001 to add NMP to the list of substances known to cause cancer or reproductive toxicity.^[1] For these compounds there are no limits. Even if a product contains minimal amounts, it has to be labelled. So, for example, if a leather containing NMP in the finish is used for a car seat, the instruction manual of the car has to include a warning label in California.^[6]

In the European Union the toxic effects and the labelling of NMP were discussed for several years. In January 2009 the classification as toxic to reproduction, Class 2, was published as an adaptation of the existing list of legal classifications of chemicals (Annex I of Directive 67/548/EEC). But when this new classification should have come into force in June 2009, the Directive 67/548/EEC, together with Annex I, was replaced by a completely new regulation 1272/2008, called CLP (Classification, Labelling and Packaging). This new regulation also covers all legal classifications from the old Annex I, but



without the latest adaptations (including NMP) because the text of the law was written before the amendments were published. Therefore the new classification was eliminated before entering into force. The latest adaptations had to be published again as amendments of CLP Regulation; this was processed in August 2009. So the actual situation in the EU is as follows:

- The Regulation 790/2009/EC with the new classification of NMP as toxic for reproduction, entered into force on September 26th, 2009. The changes have to be applied after a transition period no later than December 1st, 2010.

NMP: Labelling and the Global Harmonized System (GHS)

Under the old labelling system in Europe:

- Mixtures containing a minimum of 5% NMP have to be labelled as toxic "T", and in addition with the risk sentences R61^[7].
- With 10% NMP or more, the R36/37/38^[7] also has to be added.
- In the range of 0.1% to 5% NMP mixtures are not classified as hazardous, but NMP has to be listed in Section 3 of the material safety data sheet (MSDS).

The Global Harmonized System (GHS) will commence in December 2010, and labelled as follows:

- NMP and mixtures with 10% or more NMP have to be labelled with the symbols GHS07, ("exclamation mark"), GHS08 ("health hazard"), the signal word "Danger" and the hazard statement codes H315, H319, H335 and H360D.^[8]
- In mixtures containing 5% to 10% NMP the labelling is GHS08 with "Danger" and H360D. Between 0.1% and 5% NMP nothing changes compared to the old system.
- For mixtures in general the old system can be used until May 2015.

These different labelling requirements are set down in *Panel 4*:

Panel 4: Labelling of NMP

Content	Old European system	GHS
≥ 10 %	T; R36/37/38, R61 	H315, H319, H335, H360D   Danger
≥ 5 %	T; R61 	H360D  Danger
≥ 0.1 %	listing in MSDS	listing in MSDS

NMP and REACH

REACH is a recent law of the European Union on chemicals and their safe use. It deals with the Registration, Evaluation, Authorisation and Restriction of Chemicals. From June 1st, 2008, manufacturers and importers have to register all chemical substances produced or imported into the EU above one ton per year. The registration deadline for substances that are already placed on the market depends on the manufactured or imported quantity (December 1st, 2010, June 1st, 2013 and June 1st, 2018). The registrants have to obtain information on the physicochemical, health and environmental properties of

their substances and to determine how these substances can be used safely.

For carcinogenic, mutagenic, toxic for reproduction substances (CMR substances), such as NMP, the deadline is December 1st, 2010. This is independent of the manufactured or imported quantity, and the most extensive and expensive toxicological tests have to be performed.

NMP also fulfils the criteria for a Substance of Very High Concern (SVHC). Under REACH, SVHC will undergo an authorisation process not only for the substance itself but also for each application process.

Even if the process is accepted, it is possible that it will be restricted or forbidden in future because the ultimate aim is that these substances are progressively replaced by suitable alternative substances. So authorisation approvals will be time limited and specific to use and supplier.

Leather containing NMP

If NMP is used in leather finishing almost 90% remains in the leather after drying, but is then released over a long period of time.^[9] This means that consumer products containing these leathers will release NMP and the end customer will be exposed to it.^[6]

- The International Material Data System (IMDS) is a collective, computer-based material data system used by automotive OEMs to manage environmentally relevant aspects of the different parts used in vehicles. The base of the system is the Global Automotive Declarable Substance List (GADSL).^[10] With the introduction of IMDS, major automotive manufacturers (BMW, Daimler Chrysler, Porsche, Fiat, Ford, General Motors, Toyota, VW and Volvo) combined their lists to the GADSL. Regarding this list, since February 2009, NMP has to be declared as an ingredient if the content is more than 0.1%.
- The Blue Angel is an important German ecolabel used in the whole European Union. This label is also applicable for furniture and the base to award it is the specification RAL-UZ 38.^[11] To fulfil the requirements of RAL-UZ 38 it is not allowed to add substances which are classified as toxic T or very toxic T+. There are no limits in this regulation which means that even the smallest amounts are relevant. As NMP is classified as toxic, if added to a leather finish used for a furniture leather the furniture will not get this label.
- In California, as discussed previously, every product containing traces of NMP has to be labelled, thus every article containing a piece of leather with NMP in the finish also has to be labelled.

Technical considerations in leather manufacture

Environmental problems have driven NMP-free finishing systems, but there are also technical problems. These relate to the migration of solvents that remain in leathers after drying. In time, and especially at raised temperatures, the mobility of small non fixed solvent molecules can lead to diffusion into deeper layers of the leather. Other substances – such as fatliquors, retanning agents or dyes – that are located deep in the structure have a relatively low mobility. However, these substances may become quasi dissolved in the solvents of higher mobility. In this

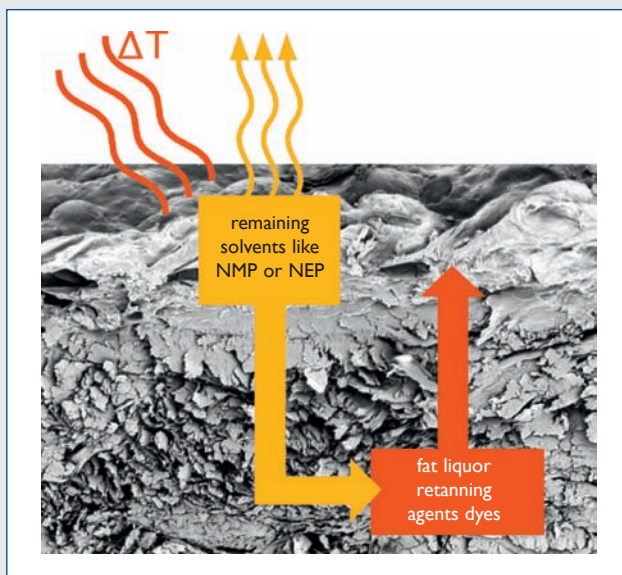


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event they can be transported to surface of the leather. This is illustrated in *Panel 5*:

Panel 5: SEM picture of a leather cross-section with an illustration of migration processes



This migration can cause change to the leather surface. For example, the leather can become greasy, uneven or dirty, or the resistance of finish fastness against mechanical stress can be reduced.

N-Alkyl-Pyrrolidones - not suitable as replacements for NMP

Higher alkyl pyrrolidones, such as ethyl, octyl or dodecyl pyrrolidone have been suggested as a replacement for NMP, and in particular the more similar N-ethyl pyrrolidone (NEP). But these are not real alternatives within leather finishing for the following reasons:

- The boiling points of higher alkyl pyrrolidones are higher than of NMP and the vapour pressures are lower. This means that they remain longer in the leather than NMP, and the risk of migration is increased.
- The higher alkyl pyrrolidones are not so well known as NMP, especially in the field of toxicology. In the case of NEP new results show developmental toxic effects on rats^[12] and nobody knows what the exposure of customers to higher alkyl pyrrolidones will mean for their health, or what the future holds for the hazardous classification of these solvents.

Sustainable elimination of NMP and VOC reduction in finishing systems

In 2001, Clariant projected to replace NMP in all leather finishing products.

The first step was to produce all polyurethane dispersions without using NMP. This was accomplished by intelligent process management and included variations of the polymer recipes to produce all binders with the same quality but without NMP, and in many cases with even less VOC.

The formulation of these new NMP-free binders to finishing products was no less challenging because numerous properties required within leather finishing had to be met. But by the beginning of 2004 Clariant leather finishing was achieved which fulfilled the high demands for automotive leather, and since mid-2005 all standard products are free of NMP.

Many problems as consequences of the omission of NMP needed to be overcome. These included the application process in leather finishing because NMP influences both the viscosity and the rheology of the products. It also affects the levelling within finish application, and the embossing of the finish.

The appearance of the leather surface can also be affected. Properties such as gloss, jet blackness, grain break, soiling behaviour or squeaking often worsen without using NMP. Fastness against abrasion, flexing or aging can also be affected.

There was no general possibility to replace NMP and fulfil all requirements. A lot of different specific solutions were necessary to surmount the production and application problems for NMP-

Panel 6: NMP and VOC content of old and new top coat recipes for automotive leather.

TOP COAT (RECIPE EXAMPLE)								
2002	Amount	NMP	VOC EU	Since 2005	Amount	NMP	VOC EU	VOC USA
Matting	400 g	7.1%	15.0%	Matting	400 g	0.0%	6.3%	6.5%
PU gloss binder 1	100 g	5.2%	6.0%	PU gloss binder 1	100 g	0.0%	0.0%	0.5%
PU gloss binder 2	80 g	7.0%	8.0%	PU gloss binder 2	80 g	0.0%	1.8%	2.3%
Silicone old	60 g	0.0%	35.0%	Silicone new	60 g	0.0%	20.0%	21.0%
Crosslinker	60 g	0.0%	20.0%	Crosslinker	60 g	0.0%	20.0%	19.8%
Water	300 g			Water	300 g			
Total	1000 g	3.9%	10.5%	Total	1000 g	0.0%	5.1%	5.3%



free products. But nowadays all kinds of leather can be produced without the need of NMP. Even automotive leather which has the highest requirements on fastness can be produced with a significantly lower amount of VOC and NMP-free. Examples are given in *Panel 6* which show the amounts of NMP in automotive finishes and the VOCs generated in 2002 compared to values since 2005.

Summary

Historically there were good reasons to use NMP in leather finishing products but findings associated with reproductive toxicity led to a new classification and labelling of NMP. The necessity to replace NMP required the development of numerous new specific ways for the synthesis of polyurethane dispersions, for the formulation of ready to use leather finishing products, and to overcome the initial application problems caused by the omission of NMP. This was a long and difficult task, but since the beginning of 2004 NMP-free finishing products have been available that fulfil customer's requirements. ☺

References:

- [1] *California Office of Environmental Health Hazard Assessment (OEHHA), The Safe Drinking Water and Toxic Enforcement Act of 1986*
- [2] *EC Directive 1999/13/EC*
- [3] *D. R. Lide; CRC Handbook of Chemistry and Physics 75th Edition 1994*
- [4] *CFR 40, Part 51.100(s), US EPA*
- [5] *e.g.: TA Luft, 01.10.2002, Bundesumweltministerium, Germany*
- [6] *N. J. Cory, JALCA 2002, 97, 496*
- [7] *R61: May cause harm to the unborn child.
R36/37/38: Irritating to eyes, respiratory system and skin.*
- [8] *H315: Causes skin irritation.
H319: Causes serious eye irritation.
H335: May cause respiratory irritation.
H360D: May damage the unborn child.*
- [9] *Wenzel W., World Leather Vol.15/8 (2002), pg.46*
- [10] *The actual GADSL can be found on the GADSL Homepage:
http://www.americanchemistry.com/s_plastics/blank.asp?CID=1106&DID=9290*
- [11] *http://www.blauerengel.de/en/products_brands/search_products/produkttyp.php?id=245*
- [12] *A. M. Saillenfait, F. Gallissot, J. P. Sabaté; J. Appl. Toxicol. 2007 Sep-Oct, 27(5), 491*