

ECOLOGICAL TECHNOLOGY: NMP-FREE LEATHER FINISHING**

by

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ABSTRACT

There were historically good reasons to use N-Methylpyrrolidone in leather finishing products, but compelling reasons to discontinue its use are now well known. Findings of reproductive toxicity lead to a new classification and labelling of NMP. 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. This was the first toxicological listing of NMP but since then others have adopted legal restrictions, e.g. in the European Union. The current regulations of these compounds offer no limits. Even if a product contains minimum amounts of NMP it has to be labelled. So, for example, if a leather containing NMP in the finish is used for a car seat in California the instruction manual of the car has to include a warning label. When NMP is used in leather finishing almost 90% remains in the leather after drying, but is gradually released over a long period of time. This means that consumer products containing these leathers will release NMP and the end-user customer may be exposed to it.

At an early stage Clariant realised that the use and acceptance of NMP must come to an end and that it will be a big and time-consuming challenge to replace it. So in 2001 our company started a research project for the replacement of NMP in all leather finishing products.

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-free products. But, starting at the beginning of 2004, Clariant offered NMP-free finishing products that fulfilled even the high demands for automotive leather while meeting the new environmental requirements. By mid-2005 all of our standard products were free of NMP.

RESUMEN

Existían históricamente buenas razones para usar N-Metilpirrolidona [NMP] en productos de acabado de cuero, pero poderosas razones para discontinuar su uso son bien conocidas. Los resultados de toxicidad reproductiva llevaron a una nueva clasificación y etiquetado de NMP. Este nuevo conocimiento llevó al estado de California, en junio de 2001, para agregar NMP a la lista de sustancias que se sabe causan cáncer o toxicidad reproductiva. Esta fue el primer listado a cerca la toxicología de NMP, pero desde entonces otros han adoptado las restricciones legales, por ejemplo, en la Unión Europea. Las regulaciones actuales de estos compuestos no ofrecen límites. Incluso si un producto contiene cantidades mínimas de NMP debe ser tal etiquetado. Así, por ejemplo, si un cuero conteniendo NMP en el acabado se utiliza para un asiento de auto en California, el manual de instrucciones del automóvil tiene que incluir una etiqueta de advertencia. Cuando NMP se utiliza en el acabado del cuero casi el 90% permanece en el cuero después de secarse, pero se libera gradualmente durante un largo período de tiempo. Ello significa que los productos de consumo que contienen estos cueros emitirán NMP y el usuario final puede estar expuesto a ella.

En una fase temprana Clariant se dio cuenta de que el uso y aceptación de NMP debería llegar a su fin y que será un gran reto y requerirá mucho tiempo para reemplazarlo. Así que en 2001 nuestra empresa inició un proyecto de investigación para la sustitución de NMP en todos los productos de acabado del cuero.

No había en general posibilidades para sustituir NMP y cumplir todos los requisitos. Una gran cantidad de soluciones específicas fueron necesarias para superar los problemas de producción y aplicación de los productos libres de NMP. Pero, a partir de principios de 2004, Clariant ofrece productos de acabado libres de NMP que cumplen con las más altas exigencias de los cueros para automóviles cumpliendo también con los requisitos del medio ambiente. A mediados de 2005 todos nuestros productos estándar estaban libres de NMP.

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INTRODUCTION

N-Methylpyrrolidone (NMP) was a popular solvent used in the leather industry for a long time and for lots of reasons. It eased the production of binders and the application on leather in many ways. So it was a very helpful ingredient to achieve good performance on leather.

But then NMP was found to be reproductive toxic and on June 15, 2001 the state of California added NMP to the list of chemicals known to cause cancer or reproductive toxicity regarding to the so called Proposition 65.¹ This was the first toxicological consideration of NMP by law and other restrictions followed. Clariant always has the ambition to develop their products in a sustainable way and to improve them not only concerning quality and usability but also in matters of health and environment.² So we started already in 2001 to work on a project to eliminate NMP in all leather finishing products. The aim was not only to replace NMP by other solvents but to reduce also the content of volatile organic compounds (VOC).

The following article shall explain where we came from using NMP and what the challenges were, what the new classification of NMP is and how the new age of NMP free leather finishing looks like.

THE BENEFIT OF NMP

Water based polyurethane binders have excellent properties for leather finishing. One problem in their chemical synthesis is the strongly rising viscosity by proceeding reaction if it is made in pure substance. The use of an additional solvent which is distilled off later on causes higher costs and is ecologically not beneficial. The necessary distillation at the end of the process needs more energy, more production time and means a loss of reactor capacity. So often a high boiling solvent is used in an amount that the viscosity gets just manageable. Higher boiling solvents have the main disadvantage that they remain in the product. Thus a non reactive and non toxic compound with high flash point has to be used which has good solubility properties to polyurethanes and lower the viscosity very effective in low amounts.

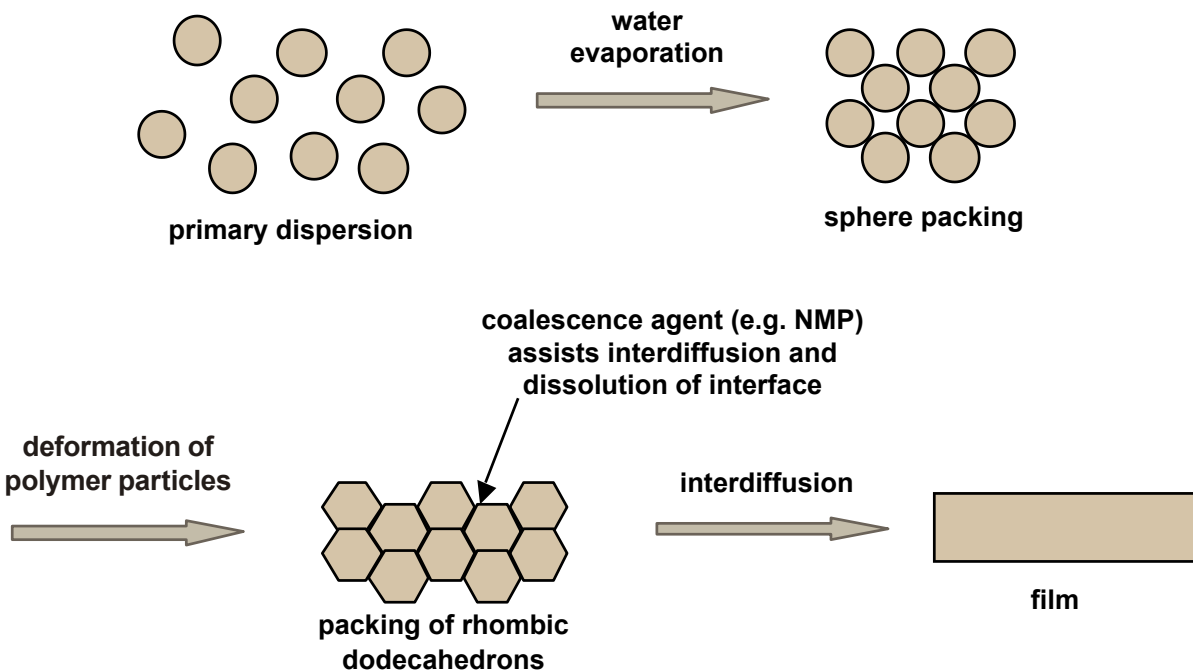


Figure 1. Film formation process

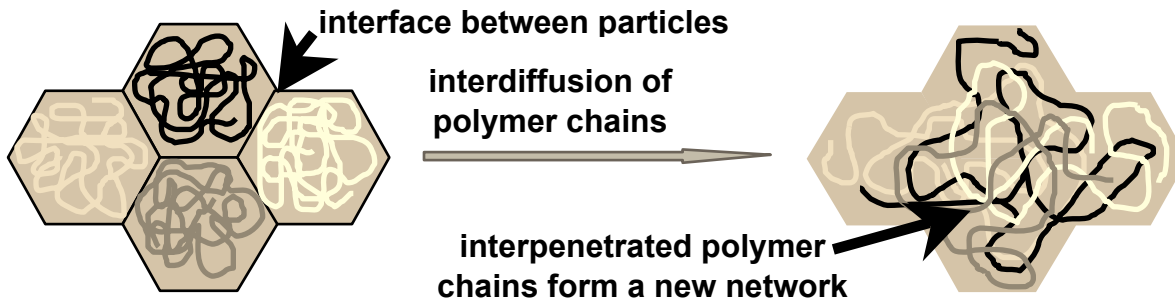


Figure 3. Interdiffusion of polymer chains.

Until NMP was thought not to be hazardous it was an ideal candidate with all these characteristics. Additionally NMP has positive effects on film formation of polymer binders (figure 1) and therefore on a lot of features of the leather coatings. When aqueous polymer dispersions are drying the water evaporates until the dispersion particles form a closest sphere packing. With further evaporation of water the polymer particles begin to deform. When all the water is gone they fill out the complete space with a packing of rhombic dodecahedrons. Between these particles still exists a kind of interface which has to be dissolved 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 (figure 3). Bit by bit the polymer chains diffuse into each other and form a new network which gives the polymer film its mechanical properties like fastness and elasticity. This process is supported by coalescence agents like NMP. These substances 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 gets easier. This means for example that the minimum film forming temperature is sinking with coalescence agents.

In the application on leather NMP can cause some positive effects especially when the complete system is a little bit critical. To name just a two of the effects: the levelling can get more even, the jet blackness can get better.

Until now only little spoke against the use of NMP and the advantages prevailed. It is chemically stable, completely soluble in water, miscible with a broad range of organic substances and neutral in pH. But the new toxicological aspect changed this situation completely and the trend to reduce VOC boosts this.

TOXICOLOGICAL AND VOC PROBLEMS OF NMP

Before discussing about VOC (volatile organic compounds) we have to define what this means. In Europe and the USA the definitions differ considerably. Europe classifies organic compounds as VOC if their vapour pressure at 20°C or at application temperature respectively is more than 0,1 hPa.³ The vapour pressure of NMP at 25°C is 0,4 hPa,⁴ so it belongs to VOC regarding to the European definition. In the USA VOC are chemical compounds that take part in photochemical reactions in the atmosphere.⁵ 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 such substances respectively as much as possible to minimize pollution of air and environment. Therefore the legislators reduce the limits for emissions of such compounds step by step.⁶ To be able to follow these moving limits the use

of these substances has to be reduced or money has to be investigated into more and 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 for 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 minimum amounts, it has to be labelled. So for example if a leather containing NMP in the finishing is used for a car seat the instruction manual of the car has to include a warning label in California.⁷

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 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 covers also 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 adaptations have been published. Therefore the new classification was eliminated before entering into force. The latest adaptations had to be published again as adaptations of CLP Regulation; this was processed in August 2009.

So the actual situation in the EU is the following: The Regulation 790/2009/EC with the new classification of NMP as toxic for reproduction entered into force on September 26th, 2009, and the changes have to be applied after a transition period latest on December 1st, 2010.

NEW LABELLING, GHS AND REACH

Regarding to the old labelling system in Europe NMP as a pure substance and mixtures containing a minimum of 5% NMP has to be labelled as toxic "T" and additionally with the risk sentences R61.⁸ With 10% NMP or more the R36/37/38⁸ has to be added, too. 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).

In December 2010 the new Global Harmonized System (GHS) will start. According to GHS NMP and mixtures with 10% or more NMP have to be labelled with the symbols GHS07 (exclamation mark) and GHS08 (health hazard) the signal word "Danger" and the hazard statement codes H315, H319, H335 and H360D.⁹ 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 Mai 2015.

REACH is a new law of the European Union (EU) on chemicals and their safe use. It deals with the **R**egistration, **E**valuation, **A**uthorisation and **R**estriction of **C**hemicals. 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 CMR substances (carcinogenic, mutagenic, toxic for reproduction) like NMP the deadline is December 1st, 2010, independent on the manufactured or imported quantity and the most extensive and expensive toxicological tests have to be performed.

NMP fulfils also 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 first 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 authorization approvals will be time-limited and specific to use and supplier.

Thus, for example it will be very difficult to get an authorisation for an application process like spraying of a cmr substance like NMP with a spray gun!

LEATHER CONTAINING NMP

If NMP is used in leather finishing the main amount (almost 90%) remains in the leather after drying and it is released for long period of time.¹⁰ So even the end products will release NMP and the end customer will be exposed to it.⁷

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).¹¹ With the introduction of IMDS, BMW, DaimlerChrysler, Porsche, Fiat, Ford, General Motors, Toyota, VW and Volvo combined their lists to the GADSL. Since February 2009 regarding to this list 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 therefore the base to award it is the RAL-UZ 38.¹² 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 smallest amounts are relevant. As already said NMP belongs to the toxic substances. So if NMP is added to a leather finishing which is used for a furniture leather the complete furniture will not get this label. Nowadays ecolabels are getting increasingly important and the producers take more and more effort to get them. Thus also furniture producers ask for NMP free finished leathers.

As described above every product containing even traces of NMP has to be labelled in California. Thus every article containing a piece of leather made with a NMP containing finishing also has to be labelled. And nobody of the finishing producers or the leather producers is able to foresee the complete way of every piece of leather and if it will be one day in California. So the only safe way is to work without any amount of NMP. That's the reason why more and more leather producing companies ask for NMP free leather finishing products.

Beside the exposure of customers and the abiding by statutory limits the use of solvents remaining in the leather after drying can cause additionally problems by migration processes. By the time or especially at higher temperatures the mobility of small non fixed solvent molecules can lead to diffusion into deeper layers of the leather. Other substances like fat liquors, retanning agents or dyes are located there which have themselves a lower mobility. But if they are quasi solved in the solvents of higher mobility they can be transported up to surface of the leather. So the leather surface can change and unwanted effects can be the consequence. For example the leather can get greasy, uneven or dirty or the fastness against mechanical stress can go down.

DETECTION OF NMP IN LEATHER

There are different possibilities to investigate the NMP content in leather. The most important three methods which can also be used for other volatile substances will be explained here.

The static headspace is one of the simplest assemblies. The leather sample is put into a small vessel which is hermetically sealed. After heating the sample containing vessel a part of the headspace gas is taken out with a syringe and injected into a gas-phase chromatograph. There the different volatile compounds are separated, detected and identified. One main disadvantage of this method is the high temperature needed to evaporate the substances into the headspace gas. When aqueous samples are taken instead of a piece of leather we

found a lower detection limit for NMP of about 20 ppm. For solid substrates this method is of limited suitability.

The dynamic headspace is mainly used by the automotive industry and is made following the VDA 278 ("Thermodesorption analysis of organic emissions for characterisation of non-metallic materials for automobiles"). The leather piece is put into a desorption tube through which Helium is floating as carrier gas. For VOC investigations the tube is heated to 90°C for 30 min. The Helium containing the volatile compounds is cooled down in a cryo-trap to freeze out all carried substances. After that procedure the trap is heated up to 280°C and the evaporating substances are analysed by gas-phase chromatography.

The chamber method is mainly used by furniture producers. To award the ecolabel Blue Angel the results of this measurement method are important. The desorption conditions differ significantly from the methods already discussed. The used temperatures are much lower and desorption time is much longer, normally several days or months. Like in the dynamic headspace the desorbed compounds are collected and afterwards desorbed once again to be analysed in a gas-phase chromatograph.

N-ALKYL-PYRROLIDONES ARE NOT A SOLUTION

Some raw material suppliers advertise higher alkyl pyrrolidones like ethyl, octyl or dodecyl pyrrolidone as a replacement for NMP. Especially the most similar N-ethyl pyrrolidone is seductive. But if we have a closer look we will see that this is not a real alternative for leather finishing.

First of all the boiling points of higher alkyl pyrrolidones are higher than of NMP and the vapour pressures are lower. So they are remaining even longer in the leather and the risk of migration problems is rising.

The higher alkyl pyrrolidones are yet not so well known and examined like NMP especially in the field of toxicology. In the case of NEP new results show developmental toxic effects on rats.^[13] So today nobody knows what the exposure of customers to higher alkyl pyrrolidones will mean for their health and what the future will bring for the hazardous classification of these solvents.

So Clariant decided that N-alkyl pyrrolidones are not a sustainable alternative to NMP and searched for different ways to eliminate it.

SUSTAINABLE ELIMINATION OF NMP AND VOC REDUCTION IN FINISHING SYSTEMS

At an early stage Clariant realised that the use and acceptance of NMP will come to an end and that it will be a big and time-

consuming challenge to replace it. So Clariant started already in 2001 a project for the replacement of NMP in all leather finishing products.

The first step was to be able to produce all polyurethane dispersions without using NMP. This was accomplished by intelligent process management and even by variations of the polymer recipes. After a lot of trials and tests it was possible to produce all binders with the same quality but without NMP and in many cases with even less VOC.

This was an important success for the next step. The formulation of the binders to complete finishing products without using NMP was not less challenging because numerous properties had to be fit. But in the beginning of 2004 Clariant was able to make completely NMP free leather finishing which even fulfilled the high demands for automotive leather. In the middle of 2005 all standard products were free of NMP. On this long way we learned to handle many different problems that were consequences of the omission of NMP. First effects can be seen in the application process because NMP influences the viscosity and even the rheology of the products and the levelling or embossing of the coatings. Also the appearance of the leather surface can be affected. Properties like gloss, jet blackness, grain break, haptics, soiling behaviour or squeaking often worsen without using NMP. Even the fastness against abrasion, flexing or aging can be affected.

LONG TERM MARKET EXPERIENCE

But nowadays all these problems are solved and 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 significant lower amount of VOC and without NMP like shown in the examples in table 1. In the last years Clariant faced a lot of different effects on numerous customer applications with the omission of NMP and found individual ways to fulfil all their demands and expectations. This experience is indispensable to give modern tanneries the support they need to replace NMP in their finished leather products.

Clariant's prospective way will not only be to develop innovative products for new applications or better effects but also to find possibilities to realise a further reduction of the VOC content.

CONCLUSIONS

There have been good reasons to use NMP in leather finishing products, but nowadays we know better reasons not to use it any more. The findings of reproductive toxicity led to a new

TABLE 1
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%

Table I: NMP and VOC content of old and new top coat recipes for automotive leather.

classification and labelling of NMP. The replacement of this solvent was not an easy task. New ways had to be found for the synthesis of polyurethane dispersions and for the formulation of ready to use leather finishing products. Many negative effects were found by the omission of NMP and numerous trials were necessary to solve these problems. But at the end of this long way there was a NMP free product range with an even lower VOC content which fulfils all customer requirements. Today Clariant can have a look back to a long-time experience of completely NMP free leather finishing which is very successful on the market.

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R36/37/38: Irritating to eyes, respiratory system and skin.
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H319: Causes serious eye irritation.
H335: May cause respiratory irritation.
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