



SOLVENTS / RESIDUALS

Other Names Multiple

CAS Number	Substance
68-12-2	<i>N,N</i> -Dimethylformamide (DMFa)
75-12-7	Formamide
127-19-5	Dimethylacetamide (DMAC)
872-50-4	<i>N</i> -Methyl-2-pyrrolidone (NMP)

May Be Found In

- Solvent residue in synthetic leather
- Leather and textile articles particularly associated with PU coated material
- Plastic, rubber, adhesives, and printing inks
- Industry use mixture such as degreasing products for paints, varnishes and metals and adhesive

Chemicals in this category are used in manufacturing to dissolve solids before use. They are not intended to be found in the final product, but their residues are often detected and can cause product non-compliance.

Uses in the Supply Chain

DMFa is a colorless, fishy smelling liquid which is miscible with water and many other organic solvents. It is a solvent commonly used in the production of polyurethane coated materials such as synthetic leathers. It can also be used to process coatings, adhesives, plastics, acrylic fibers, PU resins, or as a cleaning solvent.

DMAC and NMP have similar uses but are less common in manufacturing than DMFa.

Formamide can be used as a solvent in the manufacture and processing of plastics or in the spinning of acrylonitrile copolymers.¹

Why Solvents/Residuals are Restricted

- DMFa is classified as toxic to reproduction (Reproductive toxic Cat 1B per EU 1272 / 2008 EC).
- The liver is the target organ for the toxicity of DMFa in humans. DMFa has low acute toxicity and is slightly to moderately irritating to the eyes and skin. Acute exposure to DMFa has been observed to damage the liver in animal studies and in humans and exposure to the skin can cause dermatitis. Chronic occupational exposure to DMFa by inhalation has resulted in effects on the liver and digestive disturbances in workers.
- Under REACH, DMFa is classified as a Substance of Very High Concern (SVHC).²
- Under REACH, DMAC is classified as a SVHC.³
- Under REACH, NMP is classified as a SVHC.⁴
- Under REACH, Formamide is classified as a SVHC.⁵

Sourcing Compliant Materials from Your Suppliers

- Contact your suppliers and explain that you require their manufactured materials to be compliant with the current AFIRM RSL limits.⁶
- Require suppliers to submit a confirmation of material compliance or a test report from a third-party laboratory.



Chemical Information Sheet

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- When materials are received, consider performing risk-based testing to ensure the current AFIRM RSL limits are met.
- Synthetic leathers made without the use of DMFa may be available. This is a current challenge for the synthetic industry and brands need to work with suppliers to fully understand the alternatives. A common solution to reducing the use of DMFa is to replace it with DMAC and/or NMP. These cannot be considered safe alternatives as the risks to the workers, the environment and to the compliance of the final product are unchanged with these substitutions.
- Water based polyurethane formulations are becoming more common and may be suitable for brand needs. Some considerations:
 - If DMFa-free synthetic leather is produced in the same facility using a conventional (DMFa-containing) processes, potential for cross contamination is likely. This cross-contamination comes primarily from the release paper so risks can be mitigated by using different release papers for each process.
 - Cross contamination may also happen when DMFa-free synthetics are stored or shipped together with DMFa-containing ones. This predominantly happens when materials are cured/aged in the same space.
- Communicate the requirement for control of solvents/residuals to upstream suppliers.

Sourcing Compliant Formulations from Your Chemical Suppliers

- For all formulations, request SDS documentation that meets current GHS requirements. Regularly check the formulations and SDSs from chemical suppliers to see if DMFa, DMAC or NMP is being used.
- Contact your suppliers and explain that you require formulations to be compliant with current ZDHC MRSI limits whenever applicable.⁷
- Communicate with upstream suppliers that formulations must meet all brand and legal limit requirements.
- Always communicate with the responsible person for chemical management at the supplier.
- Discuss with your chemical supplier whether any safer alternatives are available that are suitable substitutes for your production needs.
- Prior to procuring any formulation, the chemical properties must be reviewed to ensure that proper protective equipment, chemical storage facilities, facility engineering controls, and associated treatment/disposal facilities are appropriate for the chemical(s).
- For unknown chemical formulations, conduct testing to check for the presence of all solvents/residuals.

Safer Alternatives

- DMFa is a commonly used solvent in PU coatings and synthetic leathers. Some alternative production practices exist for creating these materials without the use of DMFa, but care should be taken to assess the alternative materials carefully, as in some cases other solvents may be used which are only marginally better than DMFa.
- DMAC and NMP are the most common substitutions and bear the same risks as DMFa.
- MEK (Methyl ethyl ketone or Butanone) is another alternative which comes with its own risks.⁸
- Appropriate engineering controls such as closed loop recycling and air handling systems, as well as proper PPE, must be utilized whenever DMFa, DMAC, NMP or Formamide are used in production.



Additional Information

- Sustainable Chemical Processes: Tools and Techniques for Solvent Selection: Green Solvent Selection Guides (23 May 2016). <https://sustainablechemicalprocesses.springeropen.com/articles/10.1186/s40508-016-0051-z>
- Sanofi's Solvent Selection Guide: A Step Toward More Sustainable Processes. <https://pubs.acs.org/doi/10.1021/op4002565>
- ECHA Draft Background Document for N,N-Dimethylformamide (DMF) https://echa.europa.eu/documents/10162/13640/5th_recom_draft_backgdoc_dmf_en.pdf
- Gaylord Chemical Company Guidance on Replacing Problem Solvents: <https://www.gaylordchemical.com/replace-a-problem-solvent-2/>
- Gaylord Chemical Company Guidance on Replacing N-Methyl-2-Pyrrolidone (NMP): <https://www.gaylordchemical.com/replace-nmp/>

References

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- ¹ Office of Environmental Health Hazard Assessment – Formamide. <https://oehha.ca.gov/chemicals/formamide>, Retrieved April 2019.
 - ² European Chemical Agency – *N,N*-dimethylformamide. <https://www.echa.europa.eu/substance-information/-/substanceinfo/100.000.617>, Retrieved April 2019
 - ³ European Chemical Agency – *N,N*-dimethylacetamide. <https://www.echa.europa.eu/substance-information/-/substanceinfo/100.004.389>, Retrieved April 2019
 - ⁴ European Chemical Agency – 1-methyl-2-pyrrolidone. <https://www.echa.europa.eu/substance-information/-/substanceinfo/100.011.662>, Retrieved April 2019
 - ⁵ European Chemical Agency – Formamide. <https://www.echa.europa.eu/substance-information/-/substanceinfo/100.000.766>, Retrieved April 2019
 - ⁶ Apparel and Footwear International RSL Management Group Restricted Substances List (AFIRM RSL) <http://afirm-group.com/afirm-rsl/>
 - ⁷ ZDHC Manufacturing Restricted Substances List (ZDHC MRSL) https://www.roadmapzero.com/mrsl_online/
 - ⁸ The National Institute for Occupational Safety and Health (NIOSH) – Methyl ethyl ketone. <https://www.cdc.gov/niosh/topics/methylethylketone/default.html>, Retrieved April 2019