

SOLVENTS

Solvents, highly volatile organic compounds, are processing aids for paints and varnishes. They help to dissolve solid color components and improve the brushability and levelling properties. After use, they are irrecoverably lost.

The largest percentage evaporates into the atmosphere. The rest ends up in the sewage (when cleaning brushes etc.) or is disposed of as household garbage, rarely as hazardous waste.

Reducing solvent consumption will save resources. However, without thoroughly assessing the consequences this might be useless.

Paints with a reduced solvent content of less than 10% are allowed to carry the “Blue Angel” label and actually release less solvent into the environment when being processed but when have to be removed for renovation these paints require the use of additional solvents because of their high durability which finally nullifies the savings (Sell, J., 1986).

Solvents are the substances in paints and varnishes mainly responsible for the toxic effects, not only during production but also during processing.

They are divided into two groups:

Natural solvents

Gum spirit of turpentine

Citrus peel oil

Synthetic solvents

Isoaliphatics

White spirit (turpentine substitute)

Product Line Analysis - A Method to Evaluate Products

To evaluate products under ecological aspects it is necessary to take a look at the product's complete lifecycle, not only part of it.

The product line describes the various stages in the life of a product. It includes anything from raw material recovery, transportation, manufacturing processes, marketing and use to after-use. Each and every stage has to be analyzed using the following criteria:

environmental impact
raw material consumption
workplace conditions
material flow (waste, recycling possibilities)
technology use
social compatibility

Recovery

Natural solvents are produced from renewable natural materials at low technical expenses in an energy-saving manner.

These materials are originated under the influence of solar radiation while consuming carbon dioxide.

Synthetic solvents, however, are produced from crude oil in several, often costly reaction steps. That's why the energy input is higher compared to natural solvents.

Furthermore, chemical non-recyclable waste is produced.

Gum Spirit of Turpentine

Depending on the way they are recovered turpentine oils are described as:

gum spirit of turpentine

pine oil

sulfate or sulfite turpentine oil.

For natural paints only gum spirit of turpentine is used. It is produced from trees of the species *Pinus* by collecting the oleoresin (balsam), eliminating coarse impurities and using a steam-distillation process. The thus obtained turpentine oil is colorless and has a characteristic odor.

Main constituents are:

α -pinene, β -pinene and, in gum spirit of turpentine only rarely, delta 3-carene.

The type of pine tree, the geographical location, and the recovery method are decisive factors for the type and amount of specific constituents of a turpentine oil.

Citrus Peel Oil

Citrus peel oils are obtained from the peels of citrus fruits (oranges, lemons, tangerines, grapefruits, limes, bergamots), usually through cold pressing.

They are e.g. a by-product of orange juice production.

The main constituent is d-limonene.

Also contained are α -pinene and β -pinene.

As with turpentine oils, type and amount of the specific constituents, the geographical location, and the recovery method are an important factor for citrus peel oil.

(Ullmann, 1981; Römpff, 1988/90, Leung. A. 1980).

Isoaliphatics

Isoaliphatics are made synthetically from crude oil in many reaction steps using isobutane, hydrogen fluoride, and butylene.

This process also produces chemical waste which cannot be reprocessed.

Isoaliphatics of 11 to 13 carbon atoms are more and more used as solvents since their flash point is above 55°C which means that no hazard warning symbol will be required.

White Spirit

White spirit is obtained through crude oil cleavage, distillation and subsequent chemical-catalytic hydrogenation.

White spirits contain different amounts of aromatics depending on DIN standards. Even so-called dearomatized qualities still have a residual content of aromatic compounds which may include ethylbenzene, toluene, and xylene. (Gerstenberger, M. and Kruse, D. 1984).

Environmental Fate Photochemical Smog, Greenhouse Effect

The greatest share of the solvents contained in paints and varnishes evaporates into the atmosphere.

Solar radiation turns hydrocarbons and nitrogen oxides into ozone which contributes to photochemical smog (Bulfani, J. 1979; Chameides, W. et al. 1988; Finlayson, B. and PittsJ. 1976).

The thus formed ozone can be found not only in highly urbanized regions but also in so-called pollution-free zones where airborne contaminants are carried via particulates.

When evaporating terpenes and other hydrocarbons from natural solvents contribute to atmospheric ozone formation just like isoaliphatics and white spirits. Due to their specific structure terpenes react faster and are also faster degraded.

Natural solvents have been taken from nature which is why they do not add to the already existing emissions of biogenic hydrocarbons.

After use as solvents they simply return into the cycle of nature.

Isoaliphatics and white spirit, however, are made from crude oil which is taken from geological deposits. So they do contribute to anthropogenic ozone formation.

In any case, solvents are degraded to carbon dioxide and water. This mainly takes place through atmospheric reactions. Degradation through microorganisms or in waste incineration plants accounts only for an insignificant share.

When natural solvents are degraded only the amount of carbon dioxide is released which has initially been taken from the atmosphere by the plant to form it. The earth's carbon dioxide balance is, thus, not affected when using terpenes.

With the use and recovery of synthetic solvents, however, carbon dioxide bound in geological deposits is reactivated and released into the atmosphere by humans with a negative impact on the earth's carbon dioxide balance.

It means that natural solvents do not contribute to the greenhouse effect while synthetic solvents do.

Health Aspects

All highly volatile, organic compounds including solvents tend to affect our health. Solvents have a more or less skin degreasing effect which may result in all kinds of skin problems.

Natural solvents may cause allergies due to their variable and multi-component structure.

A carcinogenic effect could not be documented for any of the solvents discussed.

In animal models isoaliphatics, white spirit, and d-limonene caused kidney damages and even malignant kidney tumors in male rats. This carcinogenic effect of the above mentioned substances was attributed to a carrier protein of the kidneys, formed testosterone-related in rats, which is why it is found in considerably higher concentrations in male animals than in females. This protein was not found in humans (DFG 1989, "d-limonene").

It can be taken for granted that the solvents contained in paints and varnishes may result in CNS damages in humans. This mainly concerns painters and other building trade professionals with long-term exposure to high solvent concentrations. Because of the complexity of paint and varnish compositions, the great number of solvents and solvent mixtures used, and the hard-to-retrace exposition of persons in question we only know for sure for a small number of solvents whether or not they cause damage to the human CNS. Toluene which may be a constituent of white spirit is one of the substances considered highly probable to cause such damages (Dauderer, M. 1986; Deutsche Apothekerzeitung 1989; Orbaek, P. und Lindgren, M. 1988; Triebig, G. 1986**).

The typical strong smell of highly volatile, organic compounds in paints and varnishes must, therefore, be considered a positive feature since it serves as a natural warning.

Gum Spirit of Turpentine

Turpentine oils have a strong skin degreasing effect and, in case of repeated skin contact, may cause allergic reactions such as an itching dermatitis of afflicted skin regions (Cachao, P. et al. 1986; Pirilä, V. et al. 1969).

Mainly responsible is the hydroperoxide of the delta-3-carene which makes it so important to use gum spirits of turpentine with a low content of delta-3-carene, something most natural paint manufacturers already respect. This widely helps to avoid allergic reactions.

In medicine, too, only gum spirits of turpentine with a low delta-3-carene content are used for external (rubbing) and internal (inhalation) applications (Steinegger, E. and Hänsel, R. 1988). And the Cosmetics Act of Austria even allows the use of larch turpentine oil as an ingredient in cosmetics in concentrations of up to 4.5 g/100 g in products that "remain on the skin" and in concentrations of up to 5.0 g/100 g in shower baths.

The TLV (threshold limit value) for turpentine oils of any quality is 100 ppm. A concentration of about 200 ppm may, depending on the exact composition, cause an irritation of the mucous membrane, headache or dizziness. However, from a concentration of 200 ppm the smell of turpentine oil is well perceivable which enables us to avoid any damage caused by long-term exposure. Nevertheless, this TLV is much too vague since it doesn't differentiate the qualities of turpentine oils. It is, no doubt, absolutely indispensable for sulfate turpentine oils with a delta-3-carene content of up to 70%, however, not so necessary for gum spirits of turpentine that are virtually or even completely free of delta-3-carene and consequently much less irritating to the eyes and the mucous membrane.

Anyway, this low rating also has a positive side effect since turpentine oil as a constituent of paints or vanishes now has to be declared. And that means that any person allergic to turpentine oil is able to avoid the product or take preventive action (skin protection, ventilation etc.).

Citrus Peel Oils

Compared to gum spirits of turpentine citrus peel oils rarely cause allergic reactions. Based on the August 26, 1986 Hazardous Substances Regulation citrus peel oils and d-limonene are not considered skin irritating substances (Protzen, K. 1989).

Fucocumarins contained in some oils might have a phototoxic effect, i.e. with UV radiation they may produce brown spots on the skin (Leung, A. 1980). However, this disadvantage may remain unconsidered when citrus peel oils are a constituent in the solvents of indoor paints and skin protection is used.

A carcinogenic effect could not be documented.

In order to determine the carcinogenic effect of citrus peel oils and their main constituent d-limonene numerous tests were performed but never resulted in any positive findings.

The TLV commission and also the FEMA group of experts do not consider d-limonene a carcinogenic substance and therefore added it to the GRAS (generally recognized as safe) list of substances (Bardock, G. et al. 1990; DFG 1989; Roe, F. and Field, W. 1965).

There are not TLVs neither for citrus peel oils nor for d-limonene since the data, specifically for d-limonene, available to the TLV commission are insufficient to establish a limit value. The typical strong smell of citrus peel oils serves as a natural warning just as in gum spirit of turpentine.

Isoaliphatics

No TLV has yet been established for isoaliphatics although short-term toxicology information is available. There is little know about the long-term toxicology which doesn't mean at all these substances may be considered harmless to humans and the environment.

Isoaliphatics have a slight skin degreasing effect and are, as far as is known, non-allergenic.

Isoaliphatics are virtually odorless thus missing this natural warning to avoid any damage to the organism and specifically to the CNS. This might be considered dangerous especially with view to the quick evaporation (in only about 6 hours isoaliphatics have almost completely disappeared from the paint; Leinos, 1988) and the fact that the isoaliphatics content is high in some products.

White Spirit

White spirit also has a skin degreasing effect and may cause allergic reactions.

This solvent may contain toluene and xylene residues which both are suspected to cause cancer and birth defects. It has also been proven that toluene causes damage to the human CNS (DFG, 1989; Triebig, G. 1988).

No TLV has yet been established for white spirit. The TLV commission stated it “was not yet ready to establish a TLV for spirit” and “feels only entitled” to assess the individual, relatively precisely defined mixtures of substances such as white spirit, carburetor fuels etc. “when the results of examinations of specified gasoline vapor mixtures are available” (DFG 1989).

However, this doesn't mean at all that white spirits are harmless to the human health but it does mean that a required preventive value could not be established against the power and the interests of the petroleum industry.

The typical smell of gasoline is a warning and helps to avoid damages to the CNS.

Summarized Solvent Comparison

Being natural solvents gum spirit of turpentine and citrus peel oils should be given preference over isoaliphatics and white spirit.

I. They are recovered from renewable raw materials which means they are, so to speak, only borrowed from nature. They do not add to the greenhouse effect with an additional CO₂ load.

II. The solvent manufacture and residue removal may be performed without a high energy consumption and without additional ecological disadvantages.

III. Since isoaliphatics and white spirits both dissolve natural resins only poorly they are used as solvents in natural paints in combination with gum spirit of turpentine or citrus peel oils. This means that the only argument supporting the use of synthetic solvents, namely the missing allergenic potential, is nullified in practice. For those suffering from allergies even the smallest amount of the allergene is sufficient to cause a new allergic reaction. When the ingredients are declared, those concerned may switch to alternative products (e.g. using citrus peel oil as a solvent or solvent-free products) or protect themselves by taking appropriate preventive action.

Using products with a low content of delta-3-carene may again considerably reduce the allergenic potential of gum spirits of turpentine.

The use of NON-natural substances as the main constituent in the formulation of products pretending to be natural must be considered consumer deceit.

Bibliographie

- Bardock, G., Wagner, B., Smith, R., Munro, I und Newberne, P. 1990
"15 GRAS-Substances"
Food Technology 2, 78,
Bericht der Krebsforschungskommission der WHO
Deutsche Apothekerzeitung 1989
- Bulfam, J. 1975
"Factors in Summer Ozone Production in the San Francisco Air Basin"
Science 203, 81
- Bundesgesetzblatt für die Republik Österreich
30. August 1984
337. Verordnung: Kosmetikverordnung
- Cachao, P., Menezes-Brandao, F., Carmo, M., Frazao, S. und Silva, M. 1986
„Allergie to Oil of Turpentine in Portugal“
Contact Dermatitis 14, 205
- Chameides, W./Lindsay, R., Richardson, J. und Kiang, C. 1988
"The Role of Biogenic Hydrocarbons in Urban Photochemical Smog - Atlanta as a Case Study"
Science 241, 1473.
- Dauderer, M. 1986 „Klinische Toxikologie“
ecomed Verlag
DFG Deutsche Forschungsgemeinschaft 1989
Toxikologische, Arbeitsmedizinische Begründungen
Verlagsgemeinschaft mbH Weinheim
- Finlayson, B. und Pitts, J. 1976
"Photochemistry of the Polluted Troposphere"
Science 192, 111
- Gerstenbecker, M. und Kruse, D. 1984
"Entaromatisierte und Synthetische Kohlenwasserstoffe - eine Neue Generation von Lösemitteln“
Farbe+Lack 90/1, 30
Leinos Naturfarben
Rundschreiben Nr.3, 8.6.1988
- Leung, A. 1980
"Encyclopedia of Common Natural Ingredients"
J. Wiley and Sons Inc. N.Y.
- Orbaek, P. und Lindgren, M. 1988
"Prospective Clinical and Psychometric Investigation of Patients with Chronic Toxic Encephalopathy Induced by Solvents"
Scand. Journ. Work Environm. Health 14, 37
- Pirilä, V., Kilpio, A.,
Olkonen, A., Pirilä, L. und Siltanen, E. 1969
"On the Chemical Nature of the Eczematogenic Agent in Oil of Turpentine"
Dermatologica 139, 183
- Protzen, K.-D. 1989
Kennzeichnung, Verpackung beim Umgang mit und Transport von
Citrusfruchtschalenterpenen“
Parfümerie und Kosmetik 170/5, 264
- Roe, F. und Field, W. 1965
„Chronic Toxicity of Essential Oils and Certain Other Products of Natural Origin“
Food Cosm. Toxicology 3., 311

Shell, J. 1987

„Wasserverdünnbare Anstrichstoffe – Chancen und Probleme für das Holzfenster“

Impulsprogramm Holz

Bundesamt für Konjunkturfragen, Schweiz 980/2

Steinegger, R. und Hänsel, E. 1988

„Lehrbuch der Pharmakognosie und Phytopharmazie“

Springer Verlag

Triebieg, G. 1986

"Gesundheitsgefährdungen durch Organische Lösenmittel"

Arbeitsmedizin Aktuell 18,5, 33

"Ullmanns Enzyklopädie der Technischen Chemie"

Verlag Chemie 1981, Band 22

KATALYSE

Institut für angewandte Umweltforschung

Dr. Wolfgang Linden

Engelbertstr. 41

5000 Köln 1

Telefon (0221) 235963

Telefax (0221) 24 38 20

Rechtsform: Eingetragener Verein • Bankverbindung: Postgiroamt Köln BLZ 370 100 50 -

Kto.-nr. 74 75-500.

Mitglied der Arbeitsgemeinschaft ökologischer Forschungsinstitute

