

Recycling Chemicals

The ecological and economic advantages of solvent recovery



Information from the „Initiative Qualitätsrecycling“ of the „Verband Chemiehandel e.V.“



Solvent recycling reduces waste and preserves resources

The conscientious handling of chemicals is a major target of the „Responsible Care Program“ initiated by the „Verband Chemiehandel“ (German Chemicals Trading Federation). Used chemicals, such as contaminated solvents, are in most cases potential hazardous waste and should therefore be recovered and reintroduced into the production process and only be disposed of in another manner in exceptional cases. The goal is to re-use solvent waste as production material and not just to eliminate it. This is also the philosophy behind the recycling and waste disposal legislation.

Recycling chemicals is not only important from the ecological viewpoint, it also contains a real economic benefit for the industrial user. Contaminated solvents often represent a value which justifies the recovery costs. Nevertheless, without subsidies, economically and ecologically viable solvent recycling is only possible within narrow cost limitations. One reason for this is the legal situation which in most cases treats the thermal utilisation of waste and its remanufacturing in the same manner. However, in comparison with thermal utilisation, the remanufacturing of a substance requires an enormous technical outlay before a tradable and qualitatively high value solvent is produced. Therefore, the economic feasibility of solvent recycling is determined on the one hand by the calorific value of the solvent waste and on the other hand by the market price of fresh solvent. In comparison to thermal utilisation, recycling solvent waste is becoming increasingly less common - as a recent study has demonstrated*. Although there are about 30 recycling plants in Germany with adequate capacity for solvent treatment, this branch of industry has registered a reduction in quantities of up to 30 %.

The target of the „Quality Recycling Initiative“ by the „Verband Chemiehandel“ is to reverse this trend. Every kilogram of solvent which can be attributed with a higher value by recycling in comparison with its calorific value contributes towards the preservation of our scarce resources.

*„Aufbereitung gebrauchter Lösemittel – Verwertungsanlagen in Deutschland“, Sonderabfall-Management-Gesellschaft Rheinland-Pfalz mbH, Juli 1999



Redistillation – an alternative to fresh products

Industry and the manufacturing sector require large volumes of chemicals as solvents and extractants as well as for cleaning purposes or in the production of goods. In most cases, the substances are not consumed in these processes they are merely contaminated. The used solvents must then be removed as (hazardous) waste. The methods are energetic/thermal disposal or depositing substances in a landfill. Therefore, remanufacturing contaminated solvents – a utilisation of the material – and their reintroduction to the production process preserves both resources and the environment. Indeed, many of these substances are manufactured directly from the primary raw material mineral oil or are based on compounds which are obtained from petroleum by the catalytic-cracking process.

The situation regarding the recovery of solvents varies from one industry to another. For example the consumption of antifreezing agents on a glycol basis in Western Europe is estimated at between 200,000 and 300,000 tons per year of which only about 10 % is subjected to a recycling process. In contrast, a positive example is the waste management of textile dry cleaning agents in Germany: This reduced the consumption of the chlorinated hydrocarbon perchloroethene from 20,000 tons in 1986 to currently about 2,000 tons. Today, the share of recycled perchloroethene for the cleaning of textiles amounts to roughly 70 %.

As a rule, there is no reduction in quality between recycled chemicals and the original product. The following examples demonstrate the many different uses of redistillation.





Aromatics

Manufacture and fields of use» Toluene is an aromatic hydrocarbon. Just like xylene, it is produced by splitting up – fractioning – mineral oil into its components. This chemical has a wide field of use, for example as the intermediate for the synthesis of dyes, explosives or pharmaceuticals. It is also used as the initial product for foamed plastics and synthetic fibres. When it is added to fuel, toluene increases the octane number and thus the knock resistance. Also, it is used in many manufacturing processes as a solvent.

Recycling process» Generally, used toluene is coloured and contaminated with foreign solvents, lake or resin residues. Before recycling, the liquid is thoroughly analysed. Tests are carried out to establish appearance, odour, density, boiling point and substance composition. In a first purification step, coarse foreign impurities are separated using distillation and then utilised thermally. Using a subsequent rectification – a multistage distillation process – other solvents, such as hexane for example, can also be removed.

Distillate» The reclaimed material which remains after these processes is a clear, colourless product of high purity. It can be used as a solvent or as a dilution additive.

Specifications of high grade distillates

	Toluene	Xylene
Purity (in %)*	> 99.7	> 99
Appearance	clear, colourless	clear, colourless
Water content (in %)*	< 0.04	< 0.1
Boiling point (°C)	110 – 111	137 – 139
Density (20°C, kg/dm ³)	0.865 – 0.871	0.870 – 0.871
Colour standard (Hazen)*	< 10	< 20

*Purity, water content and colour standard can be specified further.

Alcohols

Manufacture and fields of use» Isopropanol or isopropyl alcohol, usually abbreviated to IPA, is one of the most commonly used solvents. This alcohol is made almost completely from propene which is produced by cracking mineral oil. This colourless and highly inflammable substance is used particularly as a cleaning product in the electronics and glass industry as well as in metal processing and optics.

Recycling process» Depending on the application, used isopropanol is contaminated with foreign solvents and water. The impurities are separated in a multistage distillation process. The usually oily residue which remains after reclamation can be utilised thermally.

Distillate» The quality of the distillate corresponds with that of the original isopropanol. The price of recycled isopropanol is slightly lower than that of fresh substance. The distillate can be used for practically all the applications where the original chemical would also be employed.

Specifications of high grade distillates

	Isopropanol	Ethanol
Purity (in %)*	> 99	> 99
Appearance	clear, colourless	clear, colourless
Water content (in %)*.**	< 12	< 2 – 8
Boiling point (°C)	80 – 83	78 – 80
Density (20°C, kg/dm ³)	0.785 ± 0.01	0.78
Refraction index (20°C)	1.377 ± 0.01	acc. to literature
Colour standard (Hazen)*	< 15	< 10

*Purity, water content and colour standard can be specified further.

**With a suitable initial product, the water content can be considerably < 1.



Ester

Manufacture and fields of use» Ethyl acetate, also called acetic acid ethyl ester (Etac), is used as a cleaning agent and solvent in many industries such as e.g., paint and varnish manufacturing and the electronics and glass industry. It is also required in the production of explosives, films, synthetic leather and silk. There are various different processes for producing ethyl acetate, usually it is manufactured from an ethylene basis.

Recycling process» After use, ethyl acetate is contaminated with foreign solvents, solids and water which are separated in a multistage distillation process. Along with the reclaimed substance, an oily or sticky residue remains which can be put to good use however in a thermal utilisation process.

Distillate» The quality of the distillate corresponds with that of the original. The economic value of the recycling process lies both in the saving of the costs of disposal for contaminated ethyl acetate and in the lower price of the distillate in comparison with that of the new product.

Specifications of high grade distillates

	Ethyl acetate	Butyl acetate
Purity (in %)*	> 99.5	> 99
Appearance	clear, colourless	clear, colourless
Water content (in %)*	< 0.05	< 0.2
Boiling point (°C)	76 – 77	78 – 80
Density (20°C, kg /dm ³)	0.898 – 0.902	0.875 – 0.885
Refraction index (20°C)	1.372 ± 0.005	1.394 ± 0.005
Colour standard (Hazen)* < 15		< 20

*Purity, water content and colour standard can be specified further.

Ketones

Manufacture and fields of use» Acetone is one of the most frequently used solvents. It is manufactured by converting isopropanol or by catalytic oxidation of propene. The colourless fluid, which for instance gives nail-varnish removers their characteristic smell, serves as an extraction and crystallisation agent and as an important intermediate product of many syntheses. Also, the substance is used for the dehydration of microscopic specimens as a substitute for alcohol.

Recycling process» Acetone is contaminated during use with other solvents, residues from the extraction as well as paint or resin remains. In the recycling process, the foreign substances are separated by distillation. The residue can also be used thermally.

Distillate» The reclaimed acetone can be used as a solvent or a cleaning agent and for the manufacturing of diluting agents, not however for the synthesis of pharmaceuticals. The price of the recycled acetone depends on the grade of purity.

Specifications of high grade distillates

	Acetone	Ethyl methyl ketone
Purity (in %)*	> 99	> 98
Appearance	clear, colourless	clear, colourless
Water content (in %)*	< 0,6	< 1
Boiling point (°C)	56	78 – 80
Density (20°C, kg /dm ³)	0.785 – 0.800	0.800 – 0.810
Refraction index (20°C)	1.359 ± 0.005	1.379 ± 0.005
Colour standard (Hazen)* < 10		< 15, < 20

*Purity, water content and colour standard can be specified further.



Glycols

Manufacture and fields of use» Monoethylene glycol (MEG) is manufactured from ethylene oxide by heating with water under pressure. It is used in particular as an antifreeze agent as well as an additive for hydraulic brake fluids and as a vat dye ester in textile printing or as cooling agent for high performance engines. Furthermore, it is an important pre-product for polyester.

Recycling process» Depending on the application, used glycols are contaminated with brake fluid, oil or sludge and contain 60 to 70 % water. The impurities are removed by filtration and multistage distillation. The separated water can be treated in a factory-own purification plant and then fed into the sewage system. The distillation residue can be utilised thermally.

Distillate» After reclamation by distillation, the chemical can again be used as a radiator frost protection agent, as an antifreeze additive, for waste water treatment or as a solvent. Depending on the purity and water content, the price of the distillate is below that of the newly manufactured substance.

Specifications of high grade distillates

	Monoethylene glycol
Purity (in %)*	> 99.5
Appearance	clear, water-white
Water content (in %)*	< 0.1
Boiling point (°C)	196 – 198
Density (20°C, kg /dm ³)	1.113 – 1.114
Colour standard (Hazen)*	< 10

*Purity, water content and colour standard can be specified further.

Organic acids

Manufacture and fields of use» Acetic acid is a clear fluid with a pungent smell which is manufactured from methanol in a catalytic process. It is used as a solvent and as an acidification and preserving agent in the food industry. This chemical is also the initial substance for the manufacture of acetic esters – so-called acetates.

Recycling process» During acetate production, a residue of accrued acetic acid remains which is contaminated by both the end product and other chemicals. This acid must be neutralised and disposed of, i.e. either it is hazardous waste or it can be utilised in some manner. The recycling of this acid residue provides a water-clear acetic acid with a high purity grade of 98 %. In order to obtain this high quality regenerate, the exact composition of the residual acetic acid must be known and the distillation process must be continually monitored. This is essential in order to perform a complete separation of product and contaminants. As well as the reclaimed acetic acid, about 10 % contaminants remains which must be neutralised and utilised thermally.

Distillate» The reclaimed product is almost the same quality as the original acetic acid. In spite of this high quality the recycled substance can only be used in technical applications such as, for example, in the textile and leather industries.

Specifications of high grade distillates

	Acetic acid 80 %
Purity (in %)*	> 99.8
Appearance	clear, colourless
Formic acid (in %)*	< 0.2
Colour standard (Hazen)*	< 20

*Purity, formic acid and colour standard can be specified further.

Chlorinated hydrocarbons

Manufacture and fields of use» Tetrachloroethene which is also called perchloroethylene or simply PER, is a colourless liquid which is used for dry cleaning textiles as well as an extracting agent and solvent in industrial processes. The main customer is the metal processing industry with a requirement of about 3,500 tons per year which uses the substance as a cleaning agent. The basis for the manufacture of tetrachloroethene is ethene which is a product of mineral oil or natural gas. The chemical removes dirt and fat from textiles or from metal surfaces. Other chlorinated hydrocarbons with good oil and fat solubility properties are trichloroethene and dichloromethane.

Recycling process» After use, the degree of contamination of tetrachloroethene can be as high as 95 %. Depending on this, the consistency of the used substance is either fluid, doughy or even powdery. Special distillation processes are used to separate the solvent from the residues. These usually oily residues contain a tetrachloroethene share of less than 0.1 % and up to 1.5 % chlorine compounds as a result of the introduction of oils. This residue is rich in energy and can therefore be well utilised thermally.

Distillate» The reclaimed product is almost the same quality as the original but it is not suitable for use in the food industry however. The distillate is slightly less costly than newly manufactured tetrachloroethene.

Specifications of high grade distillates

	Tetrachloroethene (PER)	Trichloroethene (TRI)	Dichloromethane
Purity (in %)*	> 99.9	> 99	> 99
Appearance	clear, colourless	clear, colourless	clear, colourless
Water content (in %)*	< 0.005	< 0.01	< 0.025
Boiling point (°C)	120 – 122	85 – 88	40
Density (20°C, kg /dm ³)	1.620 – 1.625	1.445 – 1.470	1.318 – 1.325
Colour standard (Hazen)* < 15		< 15	< 10

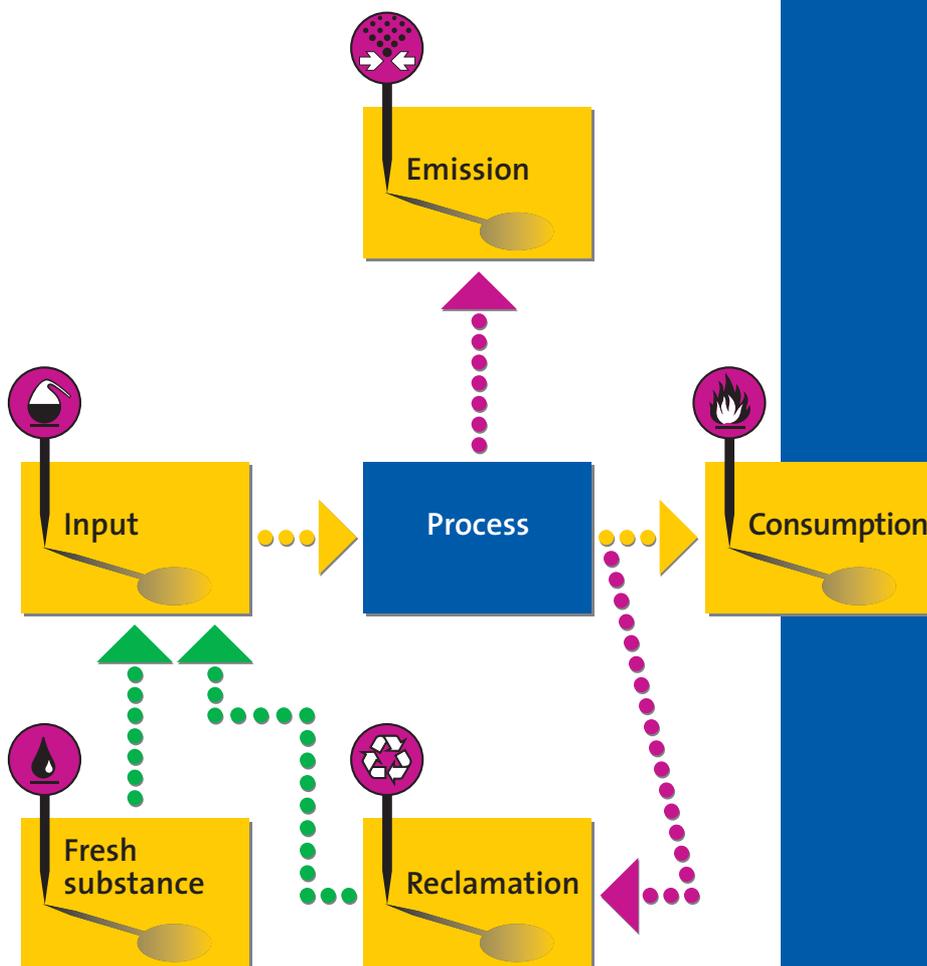
*Purity, water content and colour standard can be specified further.

» A responsible marketing of recycled chemicals starts with consultations regarding the usage of the original chemicals which are to be later recycled and culminates in the provision of comprehensive information to the users of the reclaimed products. The companies belonging to the „Quality Recycling Initiative“ offer their customers detailed product specifications on the distillates as well as comprehensive safety data sheets. The user is informed about all relevant legal obligations and safety technology data regarding the possible applications and the handling of the recycled products.

Solvent recycling combats summer smog

Volatile Organic Compounds (VOC) are the precursor substances for the formation of ozone near ground level and are therefore co-responsible for the occurrence of summer smog. From a certain level of solvent consumption onwards, the emissions fall under the European VOC directive. These require a reduction in VOC emissions by 67 % before the year 2007.

Substance recycling of VOC solvent waste reduces the overall sum of solvent consumption. In the best case, the solvent user, working together with a competent recycling company, could fall below the volume limit and the VOC guidelines would no longer apply. Then the user would no longer have to purchase expensive technology in order to fulfil the statutory emission protection requirements in a particular country - such as the Federal Emission Regulations in Germany (2. BimSchV, 10. December 1990 and 31. BimSchV, 21. August 2001).



The recycling of used solvents reduces overall solvents consumption.



Stages of solvent recycling

Control from the very beginning

Each unit of incoming used substance is exactly analysed. What was the initial product, what are the contaminants, have chemical reactions taken place? If the composition is known the solvents are prepared for distillation: solids are segregated by filtration and superfluous water is removed by dehydrating agents. By the addition of stabilisers, for example, the formation of hazardous peroxides during the distillation process can be prevented.

Analysis ensures quality

A sample of the raw product is analysed in the laboratories of the recycling company. The results of the lab analysis lead to decision which distillation process is to be used to treat the contaminated chemicals. Laboratory controls are not only carried out when goods are received but also the production process and the finished redistillate are carefully monitored in the laboratory. This ensures the highest possible quality of the recycled substances.



High towers for high purity

The distillation tower is about 20 metres high. Theoretically, there are about 30 different separation stages where the organic solvents which pass through the column can be freed from their impurities to a large extent. This distillation process is controlled by the most modern automation technology. The distillation plant of a recycler is just as effective as the production plant for fresh chemicals. Therefore, the manufacture of high quality distillate is guaranteed.



Return to the production cycle

After the purification processes, the distillates are prepared for marketing. For example, acids are diluted to the desired concentration, ethanol is denatured and the necessary stabiliser is added to tetrachloroethene. Together with its product specification and safety data sheet, the reclaimed substance can then be delivered to the customer.



The following enterprises form the „Quality Recycling Initiative“ within the Verband Chemiehandel e.V.

GALVACHEM

Galvachem GmbH, Pulheim



Rabochem AG, Murten

RE RESOLVE

Rethmann Photo - Recycling GmbH, Braunschweig



Richard Geiss GmbH, Offingen



RCN Chemie GmbH (Kruse-Gruppe), Goch



ORM Bergold Chemie GmbH & Co. KG, Bochum



Wistema Chemiehandel und Recycling GmbH, Dielheim

Impressum

Publisher »

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RCN Chemie GmbH, Goch, Germany
Wistema Chemiehandel und
Recycling GmbH, Dielheim, Germany

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Fax +49 (0)2 21-95 94 44-6
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Printed on »

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and from 50 % chlorine-free
bleached cellulose