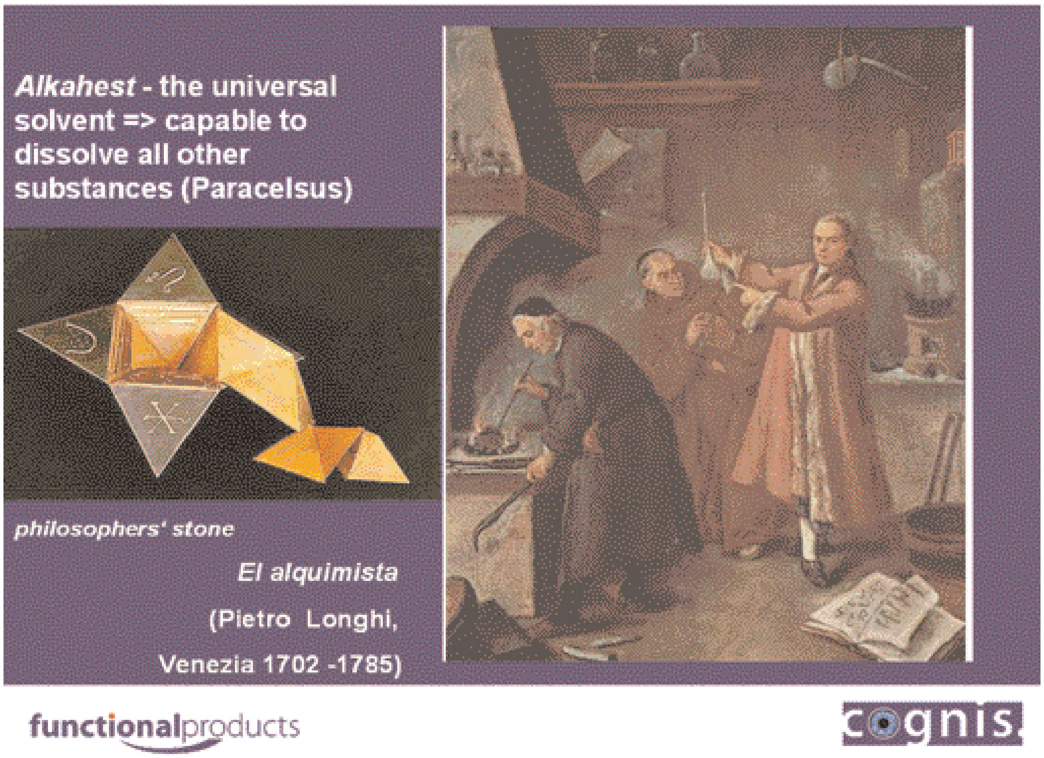

Fig. 1 - El Alquimista: a painting of Pietro Longhi, who lived in Venice from 1702-1785, and who is called the principle diarist of *Settecento* - Venice's daily life

Rainer Höfer,
Paul Birnbrich,
Stefan Busch
Cognis Deutschland GmbH & Co KG
Düsseldorf (D)
Joaquím Bigorra
Cognis Iberia
Castellbisbal (E)

SOLVENT INNOVATIONS FROM RENEWABLE VEGETABLE RAW MATERIALS

The term solvent is derived from Latin *solvens*, present participle of *solvere*, to loosen, which is exactly the function of a solvent: a solvent loosens the intermolecular bonding forces of the substance which is dissolved. Organic solvents usually have a low boiling point and evaporate easily or can be removed by distillation, thereby leaving the dissolved substance behind. Solvents should not react chemically with the dissolved compounds - they have to be inert.

Solvents appear late in the history of mankind. The early European alchemists (Fig. 1) believed that an undiscovered element existed from which all other elements descend. This hypothetical "universal solvent", called "alkahest" by Paracelsus [1], is visualized as a kind of "Ursuppe", a primordial soup, a solvent, which is capable to dissolve all other substances. Paracelsus maintained that if it were found, it would be the elixir, the philosopher's stone. So, until that time solvents still were an allegory and not in practical use.

In the 17th to the 19th century carriage coatings, the precursors of modern automotive coatings, still were slow drying varnishes of standoil cooked with natural resins like copal or amber [2] - without any solvent. Solvents, though, highlight the change from the

Paper presented at INCA Colloquia - Green Chemistry at Marghera, Venezia, 2006.

art of painting to industrial coatings. Industrial coatings as well as their cost-efficient application by spray guns only became possible, when efficient organic solvents based on acetylene-, chloro-, and nitro-chemistries were available and solvents could be used as thinners during binder manufacturing by solution polymerization and as carrier during transport and application [3].

Many modern industries have taken benefit from the development of organic solvents. With a constantly growing concern about health hazards and the environmental impact - including depletion of resources, toxicity, persistence, and bioaccumulation of chemicals - the social demand for ecologically sound solutions rose. Thus, sustainability became an increasingly important performance requirement for solvents. This applies particularly to the coating industry which consumes 46% of all organic solvents (Fig. 2) and therefore is one of the main targets for regulatory activities of legal authorities. The challenge to significantly reduce the environmental impact was anticipated with self-commitments and numerous fundamental innovations [4], and thus the requirement of sustainability leads to the development and production of "green" solvents.

Although in principle only loosening intermolecular forces the function of a solvent in industrial applications is manifold: in metal treatment solvents dissolve fat and grease and clean the metal surface, in agrochemical formulations they dissolve solid pesticides. In the preparation of coatings by definition a solvents plays only a temporary role. The solvent possibly acts as reaction medium for the synthesis of the binder, and may remain or is used to transport the dissolved binder, helps to bring it into place, allows and facilitates the formation of a coating, an adhesive film or ink dots - and should vanish finally. Volatility is a must for a solvent in coatings.

If transport is a solvent's only purpose it is also called "carrier oil". If it is intended to remain in the formulation in order to facilitate film formation it is a "coalescent", if it is due to solvate macromolecules in order to reduce the glass transition temperature (T_g) of a plastic material or a film or to form a plastisol, it is called a "plasticizer". A "solvent, which allows completion of the task, but in an environmentally conscious manner", by definition constitutes a green solvent [5]. This includes that a "green" solvent should be derived from renewable resources. Some examples of such solvents are given in Fig. 3.

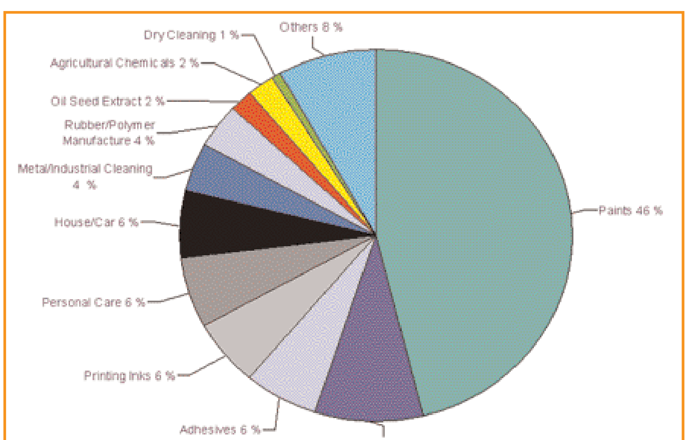

Fig. 2 - Industrial solvent applications

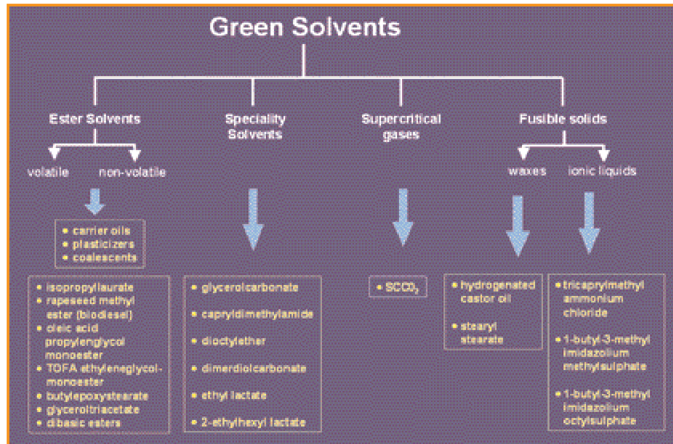

Fig. 3 - Classification of "green" solvents

During the age of petrochemistry agriculture's main focus was food crops. The production of sugar, starch and vegetable oil was mainly driven by a growing demand for human nutrition.

However, as policy priorities look towards sustainable growth using renewable raw materials, and decreasing our dependence on fossil-fuel derived feedstock, a return to a significant wider use of biomass is now possible.

This is particularly true for fuel and power generated from biomass, but the concept also hold for solvents. Whereas overall world demand for solvents is forecast to grow at 2.3% per year through 2007 and approach 20 million metric tonnes demand for hydrocarbon and chlorinated solvents will continue its downward trend as a result of environmental regulations, with oxygenated solvents and green solvents replacing them to a large extent [6]. Industrial biorefineries have been identified as the most promising route to the creation of a new domestic biobased industry (Fig. 4) [7].

A historically well known sugar-based solvent is furfural. It was first isolated in 1831 by Döbereiner. He obtained a small amount of a yellow oil as a by product in the preparation of formic acid [8]. Other chemists found the same oil by boiling vegetable materials such as oats, corn, sawdust, bran, etc., with aqueous sulphuric acid or other acids [9, 10]. In the 20th century the Quaker Oats Company, looking for new and better uses for oat hulls found that acid hydrolysis resulted in the formation of furfural. In 1922 Quaker announced the availability of several tons per month.

Furfural was first applied in large scale as solvent for the purification of wood resin. By hydrogenation of furfural, furfuryl alcohol, tetrahydrofuran or tetrahydrofurfuryl alcohol is obtained depending on the prevailing reaction conditions. All three compounds are well known as solvents.

Furfural and furfuryl alcohol are monomers which were used as basic chemicals for the production of furan resins. In 2004, the world-wide production capacity of furfural was 183,000 tons. Over the last two decades production capacity has shifted away from developed countries like the United States to currently fast developing nations. The Peoples' Republic of China has become a significant factor in the furfural production, with an estimated total capacity of 120,000 metric tons. This is equivalent to 66% of the world production in 2004. In China most of furfural is produced in small "biorefinery" plants.

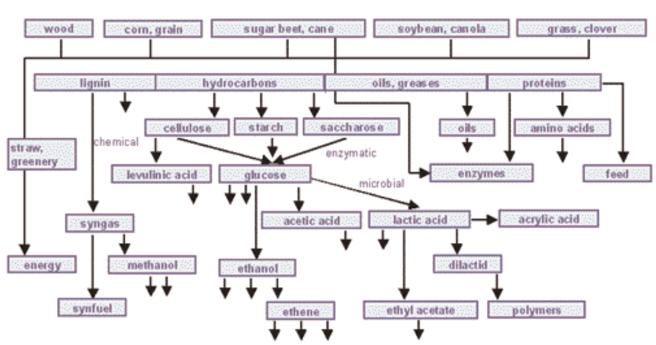

Fig. 4 - Green solvents from biorefinery processes, according to B. Kamm [7]

Another sugarbased compound is lactic acid and its derivatives. Lactic acid is produced via fermentation of starch, sugar or whey. Beside the classical use in the nutrition sector, lactic acid and its derivatives are more and more used also in the non-food sector as raw material for lactic polymers (Cargill/Dow/Kanebo), acrylates (Batelle) and green solvents (Fig. 5) [11].

Polylactic acid was first made in 1932 by Carothers, who developed a process involving the direct condensation polymerisation of lactic acid in solvents under high vacuum. Today, Cargill Dow Polymers LLC, is the leader in polylactic acid technology. A few years ago this joint venture constructed a 140,000 tpa plant to make polylactic acid (Nature Works PLA®).

Lactate esters, like ethyl lactate are regarded as environmentally benign solvents. They are non-toxic, biodegradable and show a high compatibility with other renewable materials like vegetable oils or fatty acid esters. They are mainly used as solvent or adjuvant in crop protection [12, 13].

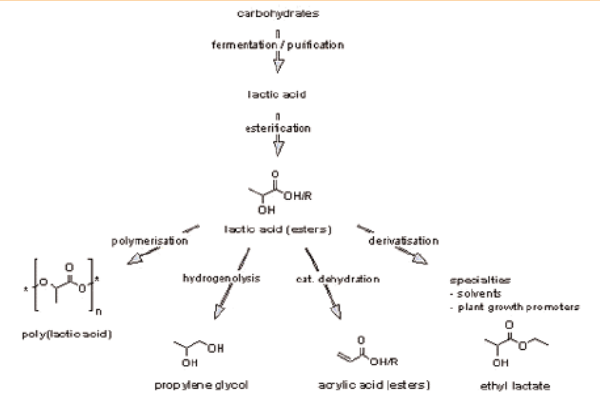

Fig. 5 - Synthesis of lactate esters and derivatives starting from carbohydrates

Another important group of renewable raw materials are oleochemicals, i.e. oils, fats, and waxes, obtained from plants and animals. The most important resources in terms of volume are soybean, palm, rapeseed and sunflower oil. The world production has increased four-fold since the 1960s (Fig. 6).

By far the largest share of the approximately 120 million tonnes produced in 2002 were used in human nutrition - oleochemical applications only consumed 18 million tonnes.

Oils and fats are triglycerides which typically consist of glycerine and saturated and unsaturated fatty acids. Triglycerides offer two reactive sites, the double bond in unsaturated fatty acid chains and the ester groups. Most oils and fats are converted to the so called oleochemical base materials, i.e. glycerol, fatty acids, fatty acid methyl esters and fatty alcohols, prior to further derivatisation or utilisation [14].

Fatty acid esters such as isopropyl laurate or rapeseed methyl ester are used in different applications as green solvents (Fig. 3). Other solvents derived from fatty acids are the dimethylamides, like capryldimethylamide [15] which become increasingly used in agrochemi-

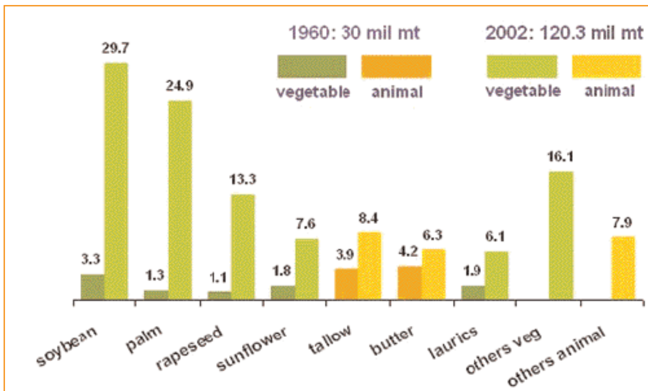

Fig. 6 - Quadrublication of oils and fats world production in four decades

cal applications. A partial substitution of classical solvents like xylene, toluene, NMP, DMF, isophoron by fatty acid esters or amides has begun. In the near future more and more petrochemical solvents will be banned due to environmental regulations. Formulators in the agrochemical business are facing a need for untoxic, environmentally friendly, high performance solvents.

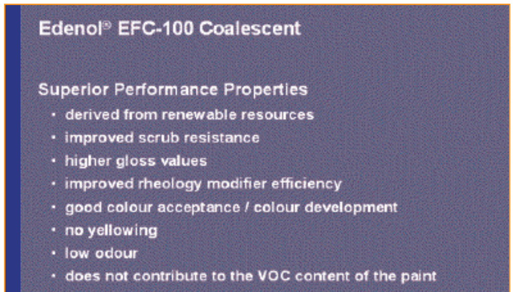

Fig. 7 - Edenol® EFC-100 as non-VOC coalescent

Fig. 8 - Comparison of market prices of some basic petrochemical solvents vs. glycerol

A good example for the development of a high-performance, yet sustainable product is the new coalescing agent Edenol® EFC-100: apart from being derived mainly from renewable (oleochemical) resources it exhibits a very high boiling point of 284 °C and therefore is not regarded as a volatile organic compound (VOCs contribute to the undesired ozone formation in the lower atmosphere. Their use will have to be reduced significantly in the near future). Edenol® EFC-100 shows an excellent performance in coating applications especially in the gloss development of the coating (Fig. 7).

With rising prices for petrochemical derived solvents their sustainable counterparts - often considered economically unattractive in the past - now become increasingly competitive. While for instance the prices of glycols have steadily risen over the last years glycerol prices have dropped significantly (Fig. 8) because this C3 alcohol is formed in large quantities as by-product of biodiesel (rapeseed methyl ester) synthesis. This situation allows the re-evaluation of many "green" solvents like glycerol, glycerol carbonate, glycerol triacetate as well as other products and concepts based on renewable resources. The future of green solvents has just begun: economic efficiency, sustainability, conservation of natural resources are terms which will emboss our near future and will support the acceptance of green solvents in the marketplace.

With the examples of new as well as reemerging "green" solvents from oleochemical or carbohydrate raw material sources the successful development of environmentally benign solvents in the sense of a sustainable development has been demonstrated.

RIASSUNTO

Solventi innovativi da materie prime vegetali rinnovabili

Il termine "solvente" deriva dal latino "solvens", participio presente del verbo "solvere", ossia sciogliere, allentare, esattamente la funzione di un solvente. Un solvente allenta le forze di legame intermolecolari della sostanza che in esso viene disciolta. Grazie al loro basso punto di ebollizione, molti solventi organici possono essere facilmente evaporati mediante distillazione, permettendo di isolare la sostanza disciolta. Altra caratteristica di questi solventi deve essere la loro inerzia chimica nei confronti del soluto.

References

[1] a) E. Davis, *Alchemy*, http://fusionanomaly.net/alchemy.html; b) A. Carrasco, *Alquimia*, http://www.monografias.com/trabajos/alqimia.shtml.

[2] R. Höfer, 6000 Jahre Sinn fürs Schöne - 6000 Jahre Lack, in 50 Jahre VILF - mit Erfahrung in die Zukunft, Schriftenreihe VILF-Vorträge, Bd. 7, 23, 2005.

[3] a) H. Gnamm, W. Sommer, Die Lösungsmittel und Weichmachungsmittel, Wiss. Verlagsges., Stuttgart, 1958; b) H. Kittel, Hrsg., Lösemittel, Weichmacher, Additive, in Lehrbuch der Lacke und Beschichtungen, Bd. III, Verl. W.A.Colomb in der H. Heenemann GmbH, Berlin, 1976.

[4] R. Höfer, S. Winkels, H.-J. Pütz, *Pitture e Vernici - European Coatings*, 2004, **16**, 28.

[5] W.N. Nelson, Green Solvents in Chemistry, Oxford University Press, Oxford, New York, 2003.

[6] The world solvents demand, Freedonia Group Ed., Cleveland, Sept. 2003.

[7] B. Kamm, P.R. Gruber, M. Kamm (Hrsg), Biorefineries - Industrial processes and products, Wiley-VCH, Weinheim, 2005.

[8] Döbereiner, *Ann.*, 1832, **3**, 141.

[9] Stenhouse, *Phil. Mag.*, 1840, **18**, 122; *Ann.*, 1840, **35**, 301.

[10] Baeyer, *Ber.*, 1887, **20**, 2811.

[11] K.-D. Vorlop, 8, Symposium Nachwachsende Rohstoffe für die Chemie, p. 23-48 Tübingen 2003.

[12] O. Toledano *et al.*, WO 2003/075657 (Makhteshim).

[13] C. Taranta *et al.*, WO 2005/074685, (BayerCropscience).

[14] H. Baumann *et al., Angew. Chem. Int. Ed. Engl.*, 1988, **27**, 41; *Angew. Chemie*, 1988, **100**, 41.

[15] S. Podubrin *et al.*, DE 195 35 483, 1995 (Henkel).