



Overview

The Industrial Solvent Market

This chapter has the objective of presenting an overview of solvents including: their history, markets, the main products and how they are inserted into some productive chains

Ana Cristina Leite
Fabiana Marra

The world of solvents is very broad and the applications are present in the daily lives of everyone. Industrial solvents represent the greatest manipulated volume and are key components in several processes and products: coatings, packaging, adhesives, cleaning products, purification of drugs, and chemicals in general, to name a few examples.

This chapter has the objective of presenting an overview of industrial solvents including: their history, markets, main products and how they are inserted in some productive chains.

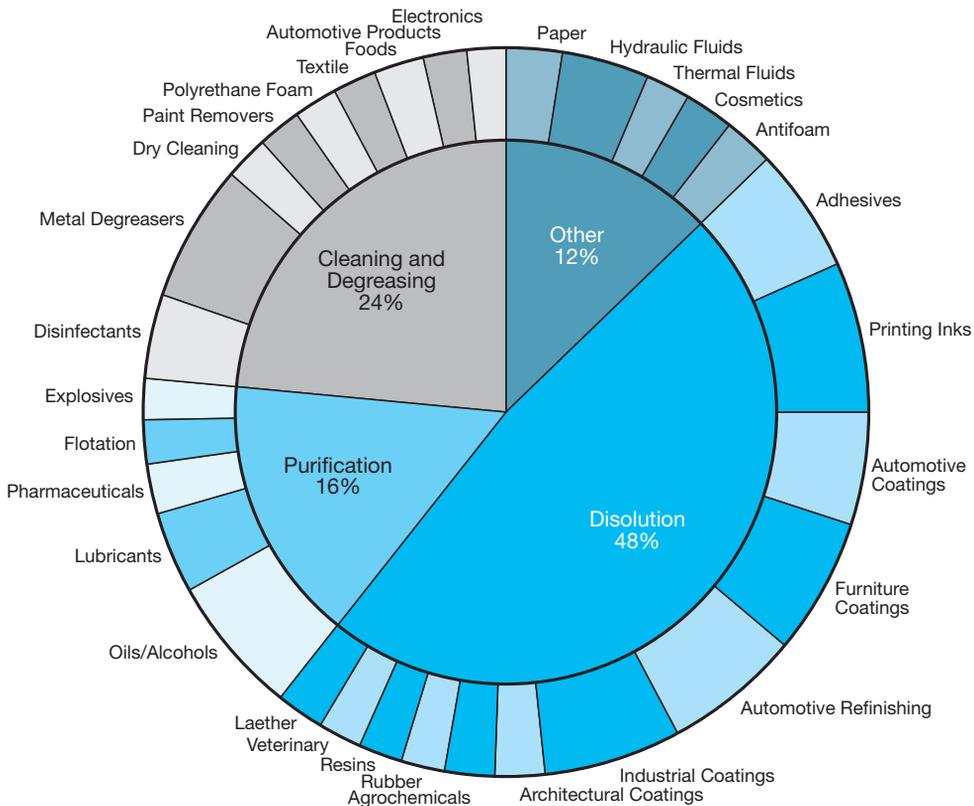


Figure 1.1. Solvents: a family of products which are present in a broad range of end markets

1.1. History

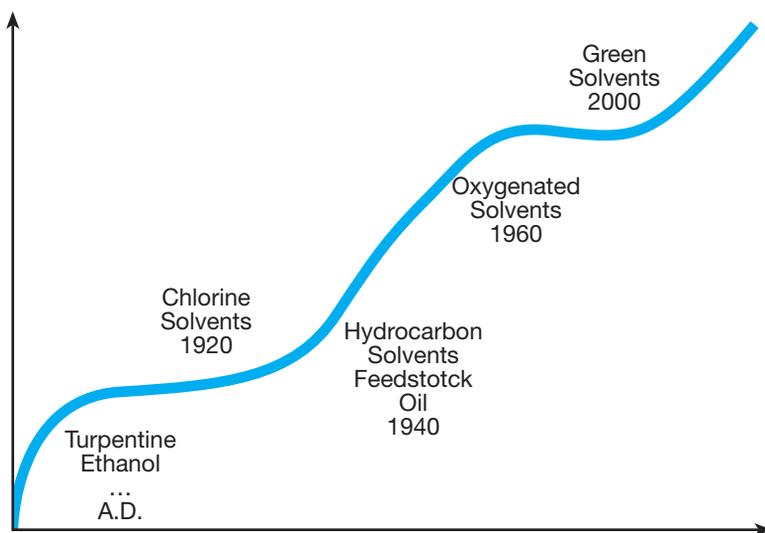


Figure 1.2. The history of solvents.

1.1.1. The Beginning

It is believed the first solvents to be used were hydrocarbons, such as turpentine, which was extracted from wood and ethanol from fermentation processes. Greek and Roman civilizations had already been fermenting grape and sugar cane for obtaining ethanol and discovered that, despite resembling water in appearance and behavior, it could dissolve oils and resins.

As early as BCE, there were records of the use of solvents for medical purposes among the Assyrians. There is also data that prove the Egyptians used them to synthesize substances for cosmetic purposes. Scientific investigations by L’Oreal chemists and Louvre scientists in Paris were conclusive in determining that the black color present in the makeup of second millennium relics was synthetic: made up of components that are nonexistent in nature.

Antoine de Chiris and Roure Bertrand Fils left their mark in the history of solvents in 1900 at the Paris World Fair, where they were awarded the grand prize for their presentation of essences extracted using volatile solvents.

The first solvent from a petrochemical source was produced in 1920.

By the end of World War I in 1918, there was a need for production on a greater scale. Coating solvents started being used to meet the demands of a market in a hurry to rebuild itself.

In the automotive industry, the introduction of machinery that enabled more agility in the painting process of cars required a faster drying process. Vegetable oil-based resins and wood resins were substituted by nitrocellulose-based resins. Interestingly enough, at the end of the war, gunpowder factories became idle and their production equipment found use in the production of these new resins.

Phenol resins came next as the first synthetic resins (1920). In 1930, alkyd resins started being commercialized.

The use of organic industrial solvents was propelled and modeled by the evolution of the type of resins and production technology of coatings. The force behind this revolution was undoubtedly a necessity of more modern fast-drying resins [1].

1.1.2. The First Wave: the Substitution Process of Organochloride Solvents

The first solvents to be produced were called organochlorides. The ICI (International Coatings Industry) was a pioneer in the production and use of these solvents.

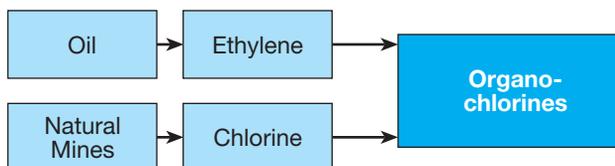


Figure 1.3. Raw materials of the main organochlorides.

The solvent trichloroethylene (TCE) was first produced in 1910, but only became relevant in applications in 1930. Carbon tetrachloride substituted gasoline in the application of cleaning materials and was considered the main organic solvent of this application until 1960, when the 1,1,1 - trichloroethane (TCA) was introduced.

Organochloride solvents were used for several years to remove wax, oils, and other substances from several surfaces. They were high performing and considered safe for workers because they were nonflammable. The most used organochlorides were: 1,1,2-trichloro-1,2,2-trifluoroethane (CFC 113), 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), tetrachloroethylene also called perchloroethylene or PERC, and also dichloromethane.

Organochloride solvents were denominated as dense non-aqueous phase liquids (DNAPL) for being odorless or tasteless and for having a higher density than water.

Despite the existing measurement techniques, organochloride solvents were not targets of detection and measurement until the 1980s. Only after analysis of residue disposal methods was it understood how these products contaminated the subsoil.

In the 1970s, scientists identified some chlorofluorocarbons (CFCs) that underwent chemical changes in the upper layers of the atmosphere leading to the depletion of the ozone layer. As a result, in 1987, 45 nations signed an agreement to restrict the production and use of these substances. In 1992, it was voted that the use of ozone-depleting substances, found in the ODSL (Ozone Depleting Substance List) Class 1, would be banned as of January 1, 1996.

Despite this, the use of substances such as CF113 and TCA, which were extremely important to the industry in metal degreasing applications, continued in the following years until alternative techniques were developed.

1.1.3. The Second Wave: the Restriction Process for the Use of Hydrocarbons

The first hydrocarbon commercialized as a solvent was benzene. In 1849, it was produced from coal and only in 1941, was it produced from oil. In the beginning, its main application was in gasoline, but by the middle of World War II, its application was extended to the chemical industry. Currently it is used mainly as a raw material in the production of ethylbenzene, cumene, and cyclohexane.

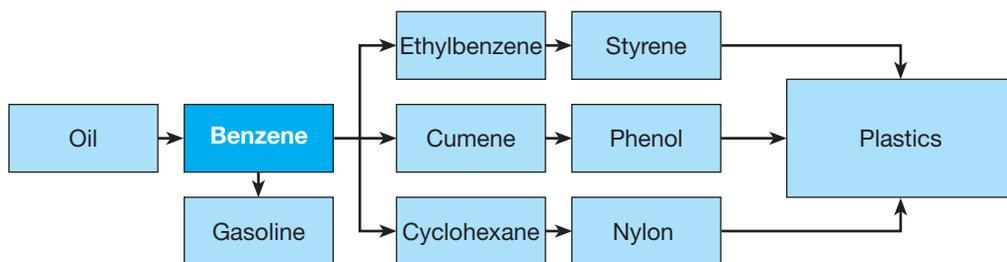


Figure 1.4. Benzene and its main applications.

In 1989 the EPA (Environmental Protection Agency) restricted the use of benzene to industrial applications. Studies were carried out on the negative health impacts that the benzene by-products, toluene and xylene, could have on workers; and the results were published in the 1990s.

Also in the 1990s, the Montreal Protocol and the Clean Air Act, one of the EPA regulations, were internationally accepted, and a gradual reduction process of ozone depleting solvents was put in place. In the United States, the emission of

volatile organic compounds (VOCs) was limited and the use of hydrocarbons, organochloride compounds, and other products were restricted in compliance with the Clean Air Act.

The industry has willingly made efforts to reduce the use of some products such as benzene, toluene, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), chloroform, and methylene chloride, for example. Environmental protection agencies are aware of these initiatives, which are mainly observed in developed countries. The greatest reduction indices have occurred in the segments of coatings and varnishes and industrial cleaning products.

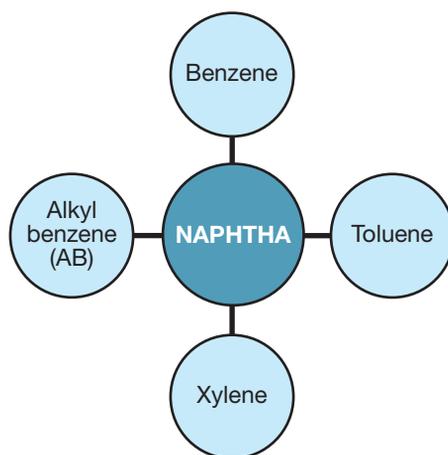


Figure 1.5. The most used hydrocarbons.

1.1.4. The Third Wave: the Evolution of Oxygenated Solvents

The evolution of the use of chemical products and their impact on human health has fueled the introduction of health, safety and environmental legislation and forced manufacturers and users to develop other kinds of products. This effort gave rise to the third wave of solvents: oxygenated solvents. In this category, there are substances with chemical functions such as alcohols, ketones, esters, glycols, glycol ethers, and others.

Before those legislations existed, more than half of the total amount of solvent-borne coatings were made from aliphatic and aromatic hydrocarbons. After the Montreal Protocol, several companies, mainly in developed countries, started substituting them with oxygenated solvents whenever it was technically possible. Currently the world consumption of industrial solvents is about 20 million tons, and 70% of those are oxygenated.

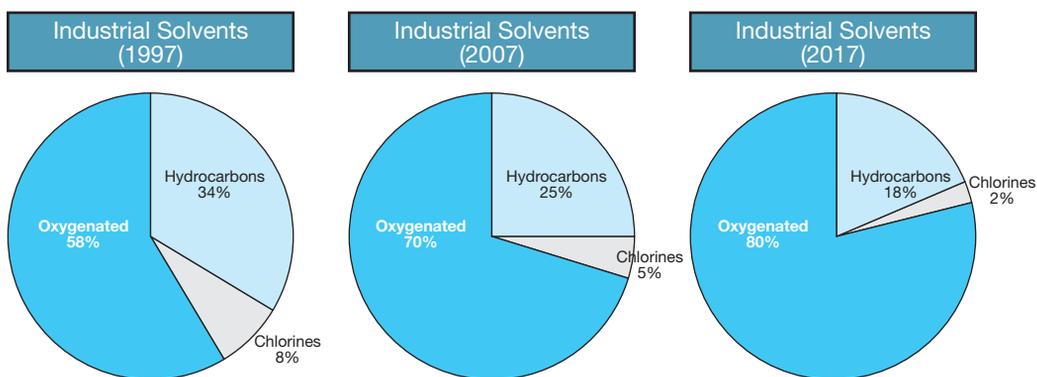


Figure 1.6. Profile of industrial solvents: organochlorides, hydrocarbons, and oxygenated (1997-2007).

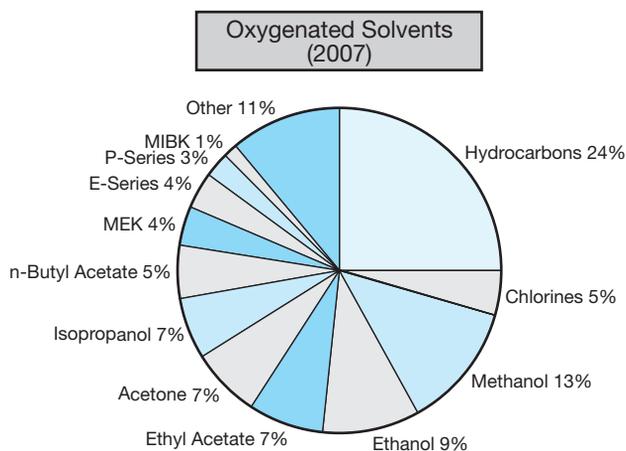


Figure 1.7. World's most consumed solvents.

1.1.5. The 21st Century: the Green Revolution

The use of petrochemical solvents is fundamental in several chemical processes and daily applications but have caused serious environmental impacts. Due to the Montreal Protocol, it has been noted the need for reevaluating chemical processes, identifying and quantifying the use of volatile organic compounds (VOCs) and their impact on the environment.

In the last decades, an increasing demand for less environmentally hazardous solvents has been noticed which has led to the creation of a new group of products: the green solvents.

The evolution of the solvent market presents, on average, the same indices as the world GDP. Although during a specific period, organochloride and hydrocarbon

solvents have had negative growth indices, oxygenated solvents have grown to twice as high as the GDP and the so-called “green solvents” have grown to four times as high.

Although the ideal solvent is yet to be found, it is necessary to search the ideal balance of efficiency, cost, and environmental impact. Some biosolvents such as methyl soyate, ethyl lactate, and D-limonene have been fairly accepted and used in several market segments for at least fifteen years.

Solvents originating from petrochemical sources, however, are predominant in the world, but growth level is directly related to hazard level for human beings and the environment.

1.2. Solvents: a Multimarket Product

As seen in Figure 1.8, due to their characteristics, solvents are used in several markets and applications.

In these markets, it is worth mentioning the coating market, not only for being the first to use solvents but for being the one which still uses them the most, be it as coatings or varnishes, printing ink, paint remover, thinners, etc.

However, in Latin America, the consumer profile presents a different distribution due to the fact that some markets are not as developed as in other regions, such as the pharmaceutical market. In this segment, solvents are basically used in the processing of active ingredients, which are mostly imported.

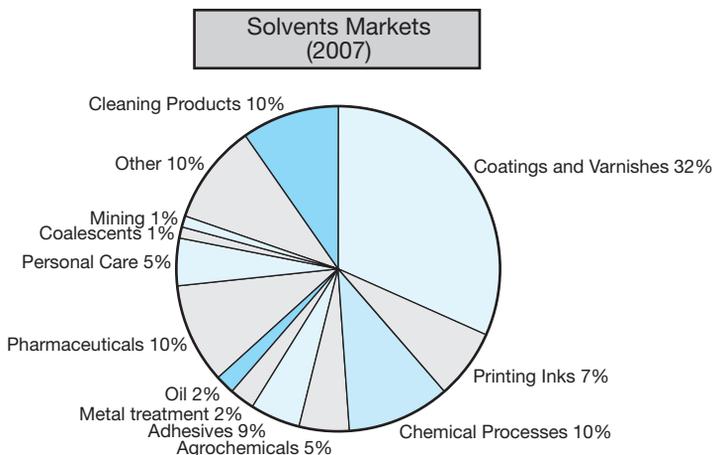


Figure 1.8. Main end markets for industrial solvents (worldwide).

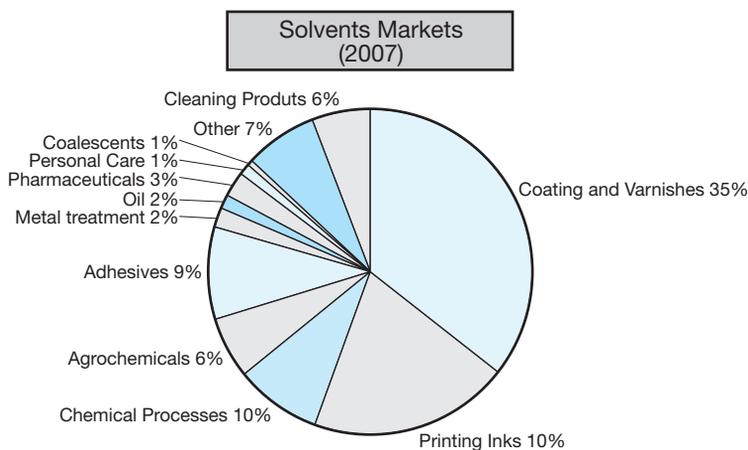


Figure 1.9. Main end markets for industrial solvents (Latin America).

1.2.1. The Coating and Varnish Market

In Europe, the United States, and Japan the coating and varnish market grows at a rate of 2% a year and is linked to the economic development of the region. In the less developed regions, market growth is around 6% per year.

It is estimated that in 2007 world consumption of coatings and varnishes was around 7 million tons.

The coating and varnish market is divided as follows:

- Decorative and Architectural Coatings;
- Automotive Coatings for OEMs (Original Equipment Manufacturers);
- Furniture Coatings;
- Industrial Coatings: (appliances, electronics, etc.).

Since the beginning of the 1970s, the majority of coatings which were produced for the architectural segment followed technology based on low solid solvents and waterborne coatings. Toward the end of the decade, pressure from laws aiming at diminishing VOCs in industrial operations, the need for saving energy and the increase of solvent cost favored the introduction of new technologies such as:

- *Waterborne* (thermocured emulsions, colloidal, and water-soluble dispersions);
- *High solids*;
- Two-component Systems;
- Powder Coatings;
- UV Cured.

These technologies experienced a strong growth in the 1990s when the *Montreal Protocol* and the *Clean Air Act* were internationally accepted.

Currently the predominant technologies are: *solventborne and waterborne*.

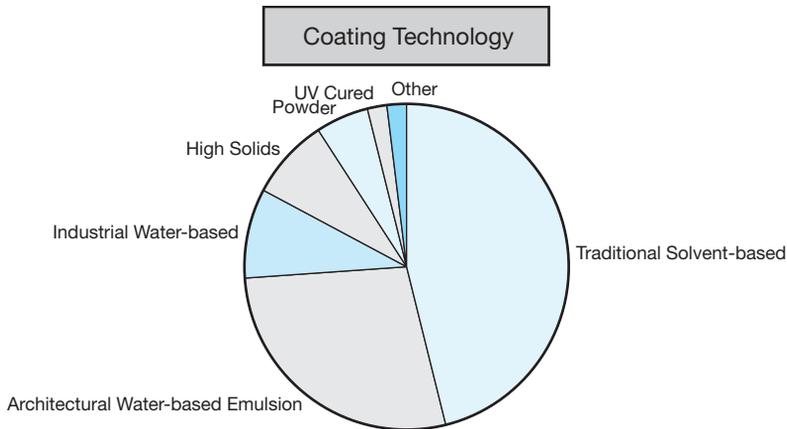


Figure 1.10. Profile indicating current technologies in the coating market.

The most highly used technology is the solventborne coating because it presents the best cost x performance relationship. It is estimated that in the next five years, legislation for air pollution will favor the growth of other technologies, such as high solids, UV cured, and waterborne.

In the United States and Europe, a consolidation of coating-producing companies is taking place; in other regions, small and mid-size producers are representing a significant portion of the market. In Asia, for example, 60% of the market is in the hands of small and mid-sized producers, while in Europe and in the United States, this figure is 20% and 35% respectively.

1.2.2. The Printing Ink Market

The printing ink market is divided into two large groups:

- printing/advertising;
- packaging industry.

The most common printing processes are: lithography, flexography, rotary printing, letterpress and screen.

The basis of excellence for the printing ink industries rests on two pillars:

- product technical quality;
- customer technical service.

This market differs from others because a large portion of the material is already sold before it is even produced. For 2007, the estimated demand was approximately 3.5 million tons, with a growth index of 4%, including the industrially developed countries.

Since it is an activity that produces a high amount of VOC emissions, it has been pressed by many legislations. However, technology changes slowly since substituting the current technologies for waterborne technology or UV-cured has an extremely high cost.

1.2.3. The Adhesive Market

There are several types of adhesives:

- waterborne;
- solventborne;
- 100% solid (*hot melt* technology and pressure sensitive adhesives);
- powder;

Adhesives have a great variety of applications in the textile industry, in flexible packaging, and in several types of structures in which it is necessary that the adhesive has high adhesion power.

This market is growing faster than the world GDP because adhesives are versatile products with the widest applications. The market has a need for products with high adhesion power because new substrates are constantly developed; be it for product design issues or for environmental issues.

Despite the fact that the adhesive industry is not among those producing the most VOCs, it still needs to adapt to new regulations.

The adhesive market may be divided according to the type of adhesive resin and the final user. Below is the market divided according to the type of resin:

- Natural Polymers;
- Water Soluble Polymers;
- Solventborne Polymers;
- *Hot melt*;
- Reactives;
- Dispersion/Emulsion.

It is estimated that in 2007 the demand for adhesives was 15.5 million tons. The segment of solventborne adhesives was third in importance and has a demand of 1.8 million tons.

In the last few years, the increasing number of regulations aiming at protecting human health and the environment have led to the decrease of consumption of solvents; for some applications, solventborne adhesives have been substituted by others produced through waterborne or hot melt technology.

New reductions in the consumption of solvents will be more difficult in the future because currently this technology is used in specific applications in which a high technical performance is required. In these cases, the substitute technologies have still not met the needed requirements.

Although the reduction of solvents is not an expected fact in the near future, in this market there is a clear trend of evaluation and substitution of current solvents by friendlier ones.

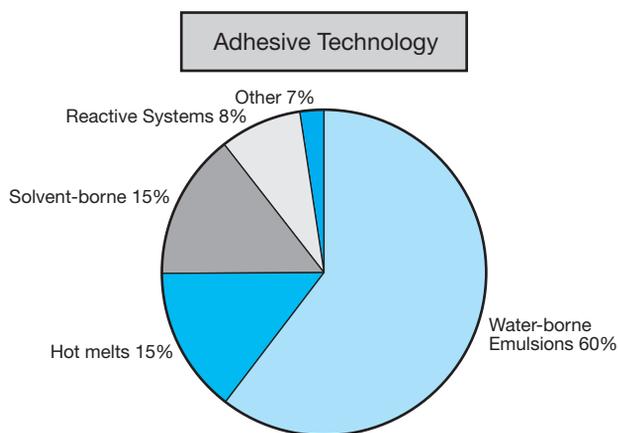


Figure 1.11. Profile of current technologies in the adhesive market.

1.3. Solvents: an Important Piece in the Petrochemical Chain

Solvents are a part of the primary product or by-product of the most important production chains of our time. Whether they are from petrochemical sources – oil or natural gas - or renewable sources, these products, are always present.

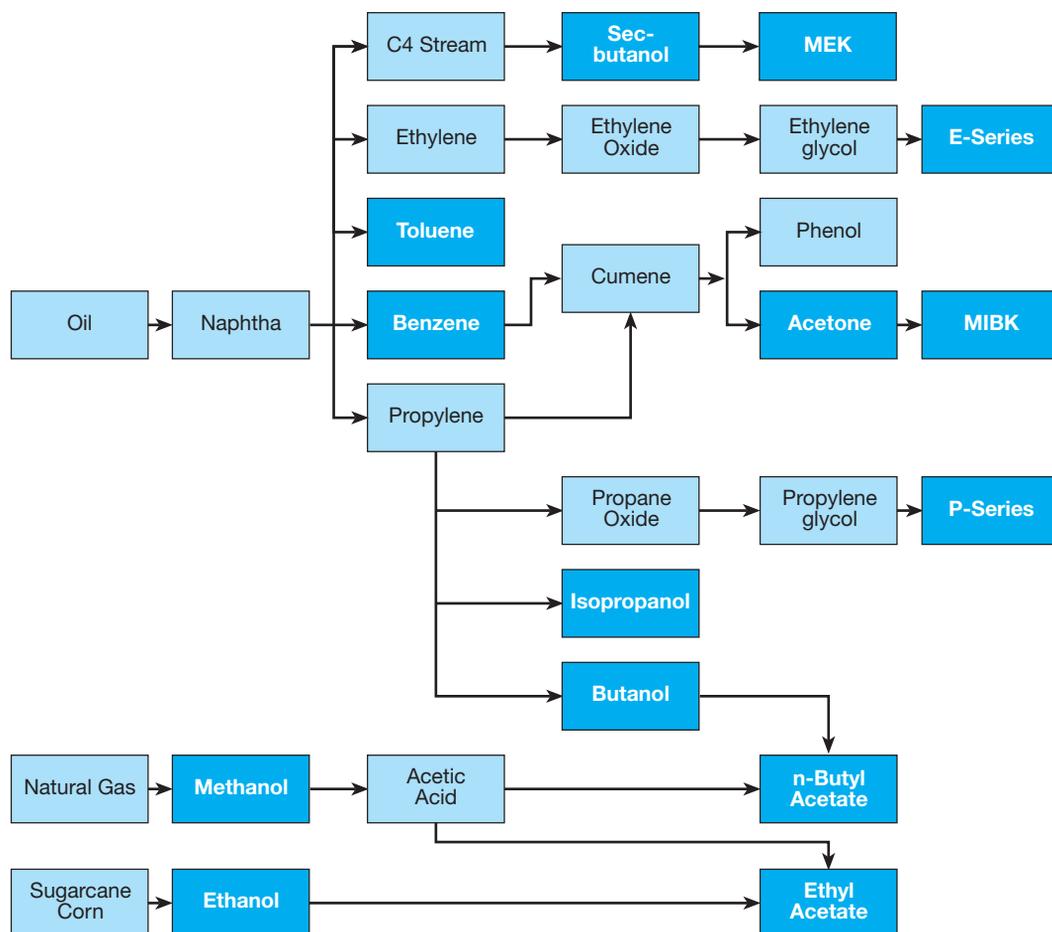


Figure 1.12. Simplified flowchart on how principal solvents are obtained.

It is important to note that some of the main molecules recognized as solvents do not have this application as the only one. Examples include acetone, methanol, and ethanol.

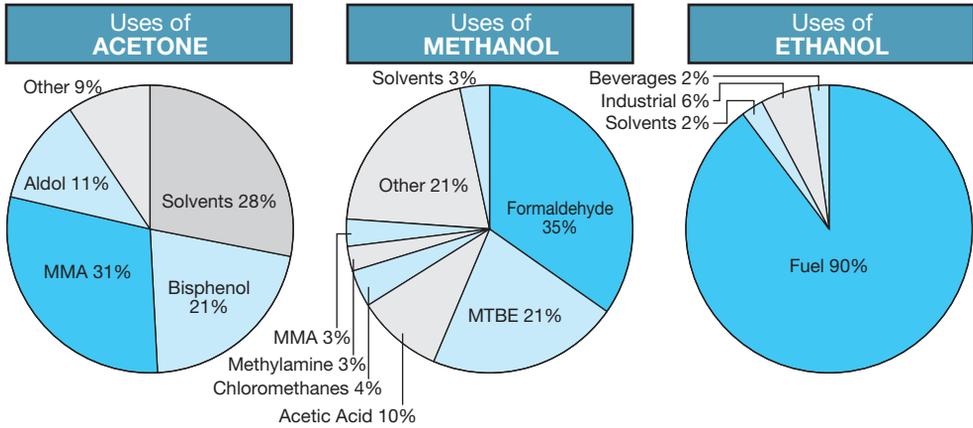


Figure 1.13. Uses of acetone, methanol, and ethanol (MMA = Methyl Methacrylate; MTBE = Methyl ter-Butyl Ether).

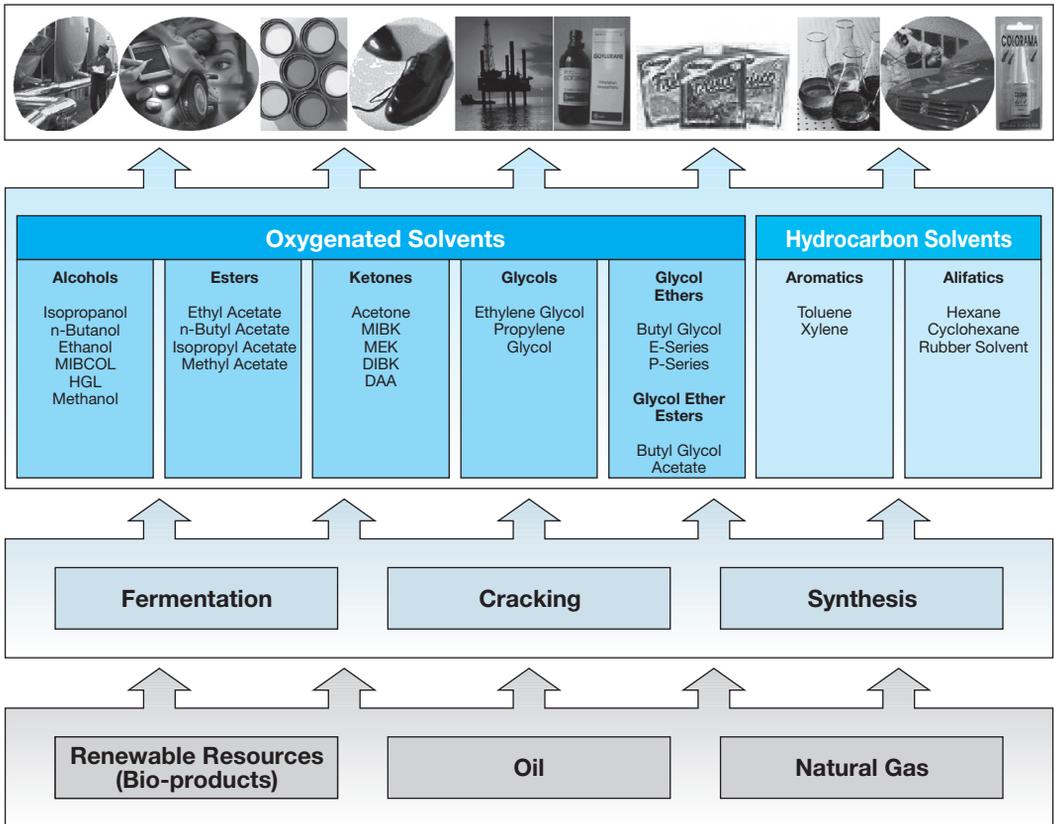


Figure 1.14. Raw materials to end markets (MIBC = Methyl Isobutyl Carbinol; HGL = Hexylene Glycol; MIBK = Methyl Isobutyl Ketone; MEK = Methyl Ethyl Ketone; DIBK = Diisobutyl Ketone; DAA = Diacetone Alcohol; IPA = Isopropanol).

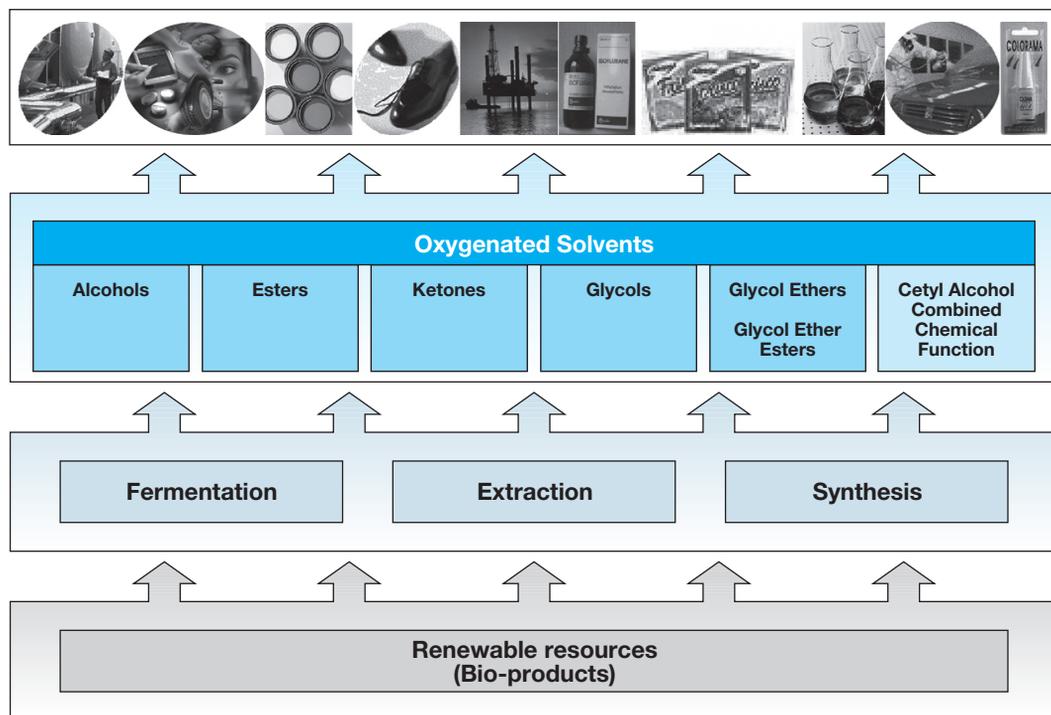


Figure 1.15. From beginning to end – a green perspective.

1.4. Solvents: Commodities and Specialties

If one is aware that the size of the world market of solvents is around twenty million tons, one may conclude that they are undoubtedly commodities, i.e., products which are commercialized in large quantities and in which producers must meet a series of requirements for operational excellence and a production scale to be a part of this market.

Some solvents are commercialized in vast quantities (more than 500,000 tons/year for each). Examples include toluene, methanol, ethanol, ethyl acetate, n-butyl acetate, acetone, MEK, and IPA (isopropanol).

Others, more than 50, are considered solvents and are commercialized in quantities that are lower than 200,000 tons/year each. Examples include diacetone alcohol, hexylene glycol, products of series E and P individually, methylisobutylcarbinol (MIBC), cyclohexanol, n-butanol, n-propanol, cyclopentanone, mesityl oxide, t-butyl acetate, isopropyl acetate, methyl soyate, ethyl lactate, n-methyl pyrrolidone, etc. The majority of these products may be considered a chemical specialty. There are few producers in the world, their production and commercialization scale are less relevant, and they normally meet

the specific needs of some applications, which makes them more of a niche application.

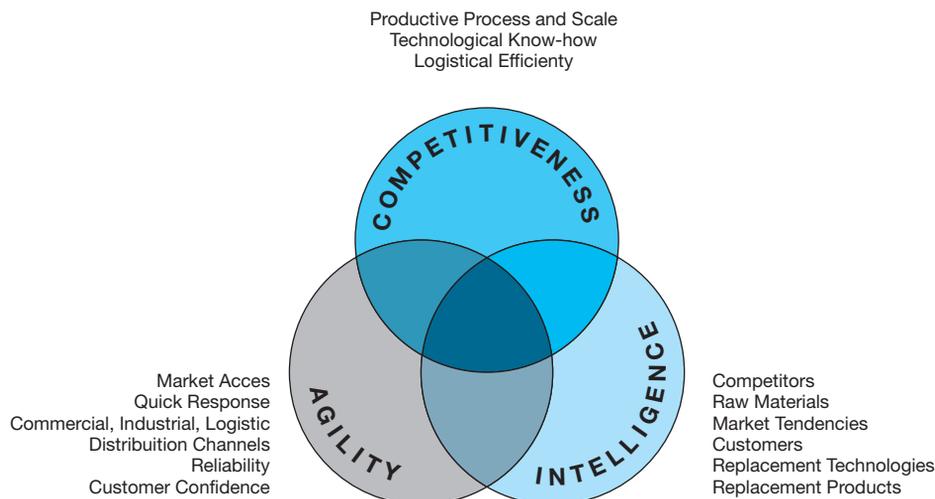


Figure 1.16. Factors all solvent products must take into account to act efficiently.

1.5. Solvents: an Old and Current Technology

Depending on the application, more than seven possible substituting technologies can be indicated.

Despite the fact that some applications have used solvents since BCE and solventborne technologies are among the oldest ones, this technology may be considered modern and current because it has evolved over the years. It came about in 1920 with the organochlorides and has evolved to meet the requirements of green chemistry and created a new class and a new concept of solvent: the green solvents, at the beginning of the 21st century.

Meeting the largest part of selection criteria: performance, cost, low initial investment, little consumption of energy in the drying and application processes, and aiming at complying with the occupational health and environmental regulations, solventborne technologies have been reborn and reinvented in this new century.

There is no ideal technology. Analyzing the history and weighing the advantages and disadvantages of solventborne technology, one may assume they will be present in the market in centuries to come.

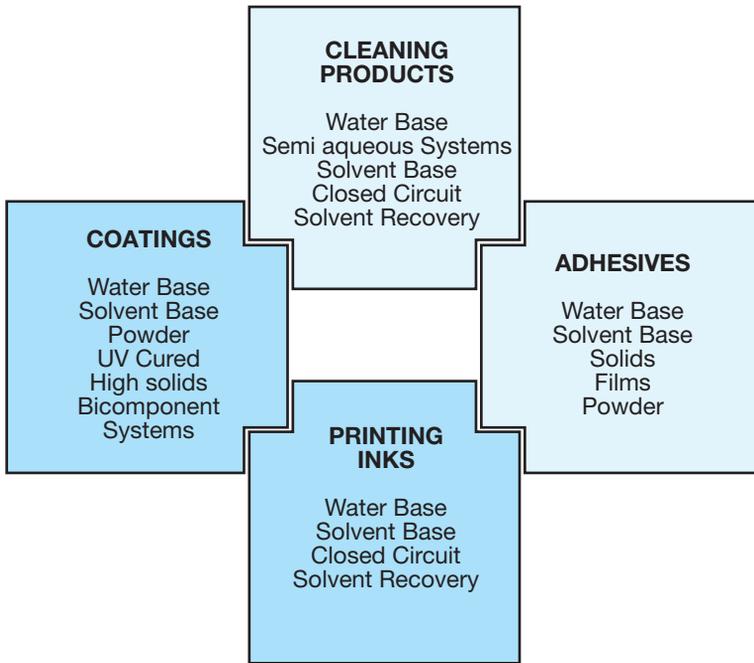


Figure 1.17. Some Replaceable Technologies.

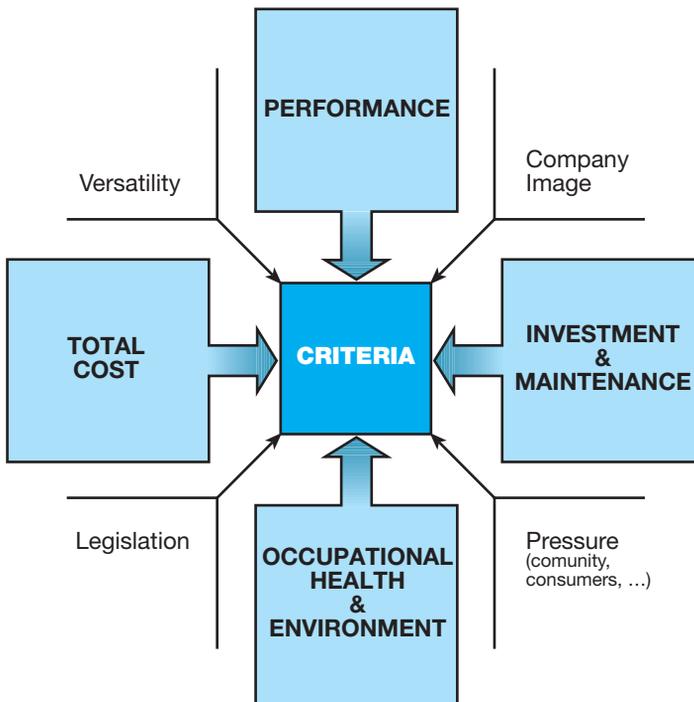


Figure 1.18. Criteria for Choosing Technology.

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