



How do the 12 Green Chemistry Principles Apply to:

*cement
manufacturing*

*organic
chemistry*

*pharmaceutical
industry*

water

*cosmetic
industry*

*carbon
fiber*

Green Chemistry Around Europe

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What is GCARE?

Green Chemistry Around Europe or GCARE as it is abbreviated is a EU project about green chemistry involving 6 schools.



Switching to clean technologies in the chemical industry, lays weight on the reduction of waste at source. This requires new technologies which have been adopted industrially. Green Chemistry has become an innovative technology since 1990 and it is constantly improving. As protection of our environment and planet has become the key issue of our age, we find it extremely important to investigate if the industry and education of our countries deal with green chemistry. We also think that it is essential to raise not only our students' but people's environmental awareness on a wider scene and this project, with carrying out international research and creating a material together with students perfectly serves this aim. The project established a Classification System to evaluate the extent the companies follow the principles of green chemistry. It examined all stages of production from the aspect of principles of Green Chemistry. Each participant carried out research in a subfield of Chemistry following specific Standards and using Eco label certificates.

In the 1st year each participant found out if the companies define green chemistry and if so, how. Furthermore the partners examined if the companies had a classification system and how it worked. They also found out if green Chemistry is part of the national curriculum of the countries. In the 2nd year results were compared and analysed and material for the Curriculum and the System of Classification was collected, selected, created and shared. In the 2nd year creative materials for dissemination were produced and the system of classification was developed.

The 12 principles of green chemistry are:

1. Prevention:

It is better to prevent waste than to treat or clean up waste after it has been created.

2. Atom Economy:

Design synthetic methods to maximize the incorporation of all materials used in the process into the final product.

3. Less Hazardous Chemical Syntheses:

Design synthetic methods to use and generate substances that minimize toxicity to human health and the environment.

4. Designing Safer Chemicals:

Design chemical products to affect their desired function while minimizing their toxicity.

5. Safer Solvents and Auxiliaries:

Minimize the use of auxiliary substances wherever possible make them innocuous when used.

6. Design for Energy Efficiency

Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. Use of renewable feedstocks:

Whenever it's possible, technically and economically, a raw material should be renewable rather than depleting.

8. Reduce derivatives:

Unnecessary derivatization should be minimized or avoided if possible.

9. Catalysis:

Catalytic reagents are superior to stoichiometric reagents.

10. Design for Degradation:

Design chemical products so they break down into innocuous products that do not persist in the environment.

11. Real-time Analysis for Pollution Prevention:

It is better to prevent waste than to treat or clean up waste after it has been created.

12. Inherently Safer Chemistry for Accident Prevention:

Choose substances and the form of a substance used in a chemical process to minimize the potential for chemical accidents, including releases, explosions, and fires.

Cele 12 principii ale chimiei verzi sunt:

1. Prevenirea:

E de preferat prevenirea formării deșeurilor decât tratarea sau eliminarea acestora după obținere.

2. Economia de atomi:

Utilizarea unor metode de sinteză care să folosească întreaga cantitate de reactanți în vederea obținerii produsului final de reacție.

3. Sinteze chimice mai puțin periculoase:

Utilizarea unor metode de sinteză a unor substanțe chimice cu toxicitate foarte mică sau chiar inexistentă atât pentru oameni, cât și pentru mediul înconjurător.

4. Obținerea unor substanțe chimice mai sigure:

Obținerea unor substanțe chimice, care să aibă efectul dorit și o toxicitate cât mai mică.

5. Solvenți și materiale auxiliare mai sigure:

Utilizarea cât mai rară a materialelor auxiliare.

6. Îmbunătățirea eficienței energetice:

Energia necesară proceselor chimice ar trebui să fie minimizată. Metodele de sinteză ar trebui să aibă loc la presiune atmosferică și la temperatura camerei.

7. Utilizarea de materii prime regenerabile:

Utilizarea de materii prime regenerabile mai degrabă decât a celor epuizabile.

8. Reducerea utilizării derivatilor:

Evitarea sau minimizarea derivatizării inutile (blocarea unor grupări funcționale, protejarea/deprotejarea, modificarea temporară a proceselor fizice/chimice), deoarece o asemenea etapă ar necesita reactivi suplimentari și deșeuri ulterioare.

9. Cataliza:

Reactivii catalitici (selectivi pe cât posibil) sunt superiori reactivilor Stoechiometrici.

10. Obținerea de substanțe chimice care să se degradeze după utilizare:

Sinteza unor substanțe chimice care să poată fi transformate în compuși inofensivi pentru mediul înconjurător.

11. Analiza în timp real pentru prevenirea poluării:

Includerea monitorizării și controlului în timp real la desfășurarea sintezelor pentru minimalizarea sau eliminarea formării de produse secundare.

12. Prevenirea accidentelor:

Metodele de sinteză a unor substanțe chimice se vor alege astfel încât să se reducă potențialele accidente chimice, inclusiv explozii, incendii și scurgeri în mediu.

What is Green Chemistry?



Many decades have passed since the publication of Rachel Carson's environmental classic *Silent Spring*. Our awareness for synthetic chemicals in the environment and their interaction with our endocrine system lead to the creation of a new approach. Green chemistry emerged in the 1990s and John Warner and Paul Anastas are coined for its foundation: they outlined 12 guidelines for working chemists in their book, *Green Chemistry, Theory and Practice*. These principles help to focus on the development of environmentally benign alternatives to hazardous chemical processes.

The costs of waste in industries, targeted research funding, tougher legislation (for our cases European Registration, Evaluation, Authorization and Restriction of Chemical substances, or REACH) and awards for best practice (Presidential Green Chemistry Challenge Awards for new ways to synthesize ibuprofen, bio-based plastics, nontoxic adhesives, water-based high-performance paint and non-toxic chemical cleaning agents) led to the quick conquer of North-American and European chemical industries by, the green chemistry movement.

A new measure '*environmental factor*' or '*E factor*' was introduced and got widely used and the product's life-cycle was also taken into consideration. The following saying crossed the borders of fantasy: "*Today's waste will be tomorrow's resource.*" Understanding what makes a chemical product safe is the challenge of green chemistry.

Rich Helling, associate director of sustainability/life cycle assessment at Dow Chemical, says his company is training its research and development scientists to do "early screening" of new products and to consider materials from a perspective of "atom and energy efficiency, hazard reduction, and holistic design," and thus "pick more sustainable projects."

"*The case for green chemistry has been made*", says Amy Cannon, executive director and co-founder of Beyond Benign, a nonprofit organization devoted to green chemistry education. "*What is next? A more systematic approach that's really going to change the way we educate scientists.*"

Teaching future chemists what makes a molecule toxic, how to spare energy and auxiliaries has reached the level of vocational education for our students.

Our understandings of green chemistry:



Green Chemistry in German is better translated as sustainable Chemistry becomes in recent decades more and more important. A variety of regulations in the European Union follow the concept of Green Chemistry as a part of the approval process of chemicals.

Thus, with the REACH Regulation 2007 a chemical legislation enacted, which makes many claims of Green Chemistry transparent and controllable. The CLP Regulation improves the information about the chemicals to the workers and consumers of chemicals. The Biocide Regulation controls since 2013 the placing of biocide products on the market.

But Green Chemistry goes beyond these regulations, since the 12 principles intended to promote sustainable development of processes and chemicals. The basic principle of green chemistry is not, to make the handling of critical products and chemicals by regulations safer, but to replace them with sustainable processes and products.



Over the past 50 years the chemical industry is developing at a rapid pace, as the oil refinery and the pharmaceutical industries have the leading part. Manufacturing processes must meet several requirements - to be safe, to include renewable energy sources, to use technologies without waste, environmentally friendly and effective at the molecular level.

The ideal product has to respond to the spending of the minimum amount of energy, to be biodegradable by microorganisms and to be reproduced. In order to maintain nature in an ecological status is necessary to educate the ideal user to use less toxic products, to separate and reduce the waste. By the "Green Chemistry" we mean safe modelling of processes and environmentally friendly chemicals.

This science studies the chemical elements, compounds, processes and their impact on the environment as toxicity, explosiveness and others. Green chemistry interacts with a number of disciplines such as microbiology, synthetic organic chemistry, biotechnology, toxicology, analytical chemistry, environmental chemistry and others. Environmental sustainability and related factors are:

1. Potential toxicity of soils
2. Potential toxicity of water
3. The potential toxicity of the food which humans eat
4. Reduction of the ozone layer

"Green chemistry" is the scientific field, which was established in 1990 and it is developing rapidly. It can be seen as art which is used to produce substances in the safest way.

The methods, used in the chemical industry subjected to this new chemistry, are not only environmentally focused, but they are also cost-effective - by cutting the stages of production and energy consumption.

In traditional chemistry scientists use multistage processes that entail a lot of waste. To solve this problem in the pharmaceutical industry they use catalysts to reduce energy consumption and chemicals.

Modern chemistry creates many new and useful products, medicines, food supplements and others which are unthinkable without the development of the civilization. Let's be responsible to nature and to ourselves and use harmless and biodegradable products in nature.



Based on the essay question of the 2006 Chemistry final written exam:

The uncontrolled development of chemical industry led to severe industrial disasters all over the world making people chemophobic and suspicious about chemistry and chemists. Meanwhile the increase of life standards had to go on. A new method, green chemistry offered a solution to ease this confrontation by the promise of products with not more toxicity than required. Moreover as time goes by, these techniques proved to be economical. Green chemistry is a twist in the scientific brain to put the nicely sounding ideas into practice.

In Europe green chemistry is called sustainable chemistry.

Based on lab experiences at secondary school level:

To do green chemistry you have to believe that there is a newer better and greener method that you will find sooner or later. Then hope that you have a stock of everything included in the recipe and the necessary equipments. Finally cross your fingers and be prepared that sometimes success is not willing to come.

According to 'Sulinet' (Hungarian official educational resource site):

'At the stage of research and development green chemistry takes the suspected environmental impacts of the future products and their productions method into consideration. According supporters and users of green chemistry, the environmentally benign and zero risk to health products and technologies are more economic on a long-term basis. In order to establish these products and technologies a change of attitude is necessary both in research and in practice.'



Starting from the 50s an optimistic view of Chemistry spread worldwide. But over the time it became clear that the chemicals that were used in manufacturing could cause serious damage to the surrounding environment and therefore to man. In fact it turned out that many of the employed substances were toxic and that industries were not taking precautions to protect the environment. For example pesticides that were well received at the beginning turned out to be of serious damage for the environment.

Other major chemical disasters were, for example: the escape of a toxic cloud in Seveso in 1976, the evacuation of a Niagara Falls area in 1978 because of buried toxic waste or the deadly fog that killed thousands of people in Bhopal in 1984. Following these tragic events, it was realized that it was necessary to regulate the chemical production through strict environmental laws in order to protect the environment and human health.

But now that chemistry is perceived as a risk, how should we behave? Is it possible to live without chemistry? Obviously not, it would for example mean to remove all plastic materials, live without Electronics and without drugs, that is to say, we would return back to the pre-industrial period.

Becoming aware of the great risks that chemical production brought with it has meant an orientation of the major industries towards sustainable chemistry. Paul Anastas and John Warner set out four basic ideas for Green Chemistry:

- Develop processes that maximize the amount of material that becomes part of the finished product in order to save raw materials and reduce waste disposal.
- Encourage industries in the use of chemicals and solvents that are safe for the environment or at least reduce their use.
- Efficient use of energy, i.e. produce as much as possible by using less energy.
- Produce less waste possible.

From these four main ideas Anastas and Warner drew up the 12 famous principles of Green Chemistry. It is important to understand that the goal of Green Chemistry is not simply the idea of cleaning up the planet, but to avoid and stop pollution in the years to come, thanks to a new plan concerning the industrial processes.

Green Chemistry ethics doesn't simply evaluate the yield of a reaction, but several criteria are taken into consideration:

- Can materials be produced from renewable sources?
- Do we produce toxic byproducts?
- Can we avoid their production?
- How much waste is produced?
- Is it energy-efficient?

The savings in raw materials and use of energy, the cost of waste disposal and the possible fines due to caused pollution are good incentives for those industries that choose Green Chemistry.

In conclusion we can say that Green Chemistry aims at helping man to make better use of chemicals and to assess what impact they can have on the environment.



Green chemistry is not a “*science*” but a state of mind, and a strategy for the future.

Green chemistry is not a straight-jacket imposed by some arbitrary certification of “*natural*”.

Green Chemistry is, however, the only way to approach the problem of dwindling resources on our planet.

Green chemistry can provide the key to lowering environmental footprints while continuing to manufacture products that consumers want at prices they are willing to pay. Green chemistry is a way of reducing the impact of a product, without necessarily changing the product itself.

Green does not necessarily mean natural. Only if a natural ingredient has been grown, harvested and treated in a sustainable way, can it be seen as a green option. In addition, synthetics can be green as long as they have been produced using green chemistry principles.

Green chemistry = measuring in the most precise way the environmental impact of each ingredient used in a cosmetic product: using the 12 principles of Anastas and Warner, because, as Lord Kelvin said: “*If you can't measure it, you cannot improve it*” (persistence, bioaccumulation, ecotoxicity, atom efficiency of synthesis, life cycle analysis...).

Green Chemistry = voicing with Prof. James Clark (York University) “*there is no such thing as waste!*” We must begin to recycle/reuse/reconfigure everything: e.g. 100 million tonnes of orange peel goes to waste every year from orange juice production, but it contains 100,000 tonnes of limonene ($\approx 1\%$), from which a good solvent could be generated in a simple chemical step which could replace a huge amount of petrochemically derived solvent.

Green Chemistry = using seaweed-derived substances to make surfactants for cosmetics.

Green chemistry = ecofriendly peptide synthesis replacing the organic solvent by a physical process (ball milling).

The conclusion is clear: in order for the Cosmetic Industry (the field of our research) to become truly “**green**”, it must replace the presently unspecific demand for “*natural*” by a systematic approach to analyse, quantify and then minimise the environmental/resource-depleting impact of each ingredient. Ingredients are not “*green*” nor “*safer*” nor “*more efficacious*” because they come from some plant, but they are “*green*” when all details of sourcing, manufacturing, disposal, including energy and water use, eco- and human toxicity are taken into account, even if “*chemistry steps*” are involved...



Scientific developments with innovations that make our lives easier in all areas continues to amaze us. All these developments might call the requirements of the modern world is not a very long history of mankind took place in almost the last 150-200 years. Of course, a lot of contributions of the umpteen alchemists in the ancient times to modern times are incontrovertible. We know that all these developments are like the steps of a ladder and boarded the peak is not one. E.g; scientific meaning of the first atomic model known as Dalton's atomic model put forth before, after, respectively, Thomson, Rutherford and Bohr atomic model did not mention the work of the modern atomic model realizations.

The mankind benefiting from a dizzying rapidly growing blessings of positive science have not unfortunately waited to meet the burden since the last one-two centuries. Benefits and harms of days to discuss the pros and cons arrived very quickly We faced a great investment and sanctions to eliminate the factors which affect our bodies directly or indirectly internally and externally so as to prevent or to minimize the impact for the work briefly for research and development R & D activities.

We are not saying scientific advances are harmful and useless, of course.

As a chemist, we only have information in this regard thanks to newspaper, the news and reviews in magazines and television. With regard to the seriousness of the job we will not lie if we said I met through this project. We are no longer in remote only of the issues that we are the audience. Someone had already taken steps in this regard. That we met talismanic issues; "12 principles of green chemistry." We learned them before. We understand what each policy as it is necessary. Yes, they should intensify efforts in light of these principles, and we should make people sensitive.

We were thrilled, to be in the project and was very gratifying to work with people in other countries have the same sensitivity. Now we are not only the audience, even though we have a little bit of business we enter into the kitchen. On the one hand developing ourselves, on the other hand, both our immediate environment we inform our students. We had happiness within us to do something nice.

In this project, our main issue was carbon fiber and associated with 12 principles of green chemistry. Carbon fiber technology is a relatively new and rapidly developing technology which enters our life. It owned by a small number of countries in the world that have this technology in Turkey as we have learned thanks to this project. What we used in our country that we are happy to observe the production of carbon fiber technology research and contacts are carried out in accordance with the 12 principles of green chemistry. We see that serious studies on this subject in our universities.

We will not forget our works we do with our students and teachers in our school lab to attention and increase the precision of the 12 principles of green chemistry. Students on this issue were worth the excitement. Each principle, that we are trustees of future generations should understand the fact that the world should be dealt with and we need to spread awareness. You do not need to explain each of the 12 individually addressed by policy. They are not difficult to achieve. These principles will be tomorrow, maybe 24 or 36, we do not know it. There are some principle similar studies in other areas other than chemistry, there will be and should be, of course.

During our studies about chemicals we used in the experiments, the reaction conditions, the formation of waste, etc. issues these principles always come to our minds. Not to waste materials, use more economic, reaction conditions suitable solvent, using a catalyst, to obtain higher yields with less energy, work according to safety principles with safe chemicals, the project and the green chemistry things do give us this 12 beautiful principles. Of course, our outlook has changed very positively

The pros and cons will always be a part of life. In the world we live well and bad, beautiful-ugly, concepts such as right and wrong is not always possible to live in a way. There are obvious negative we cannot afford, not ignoring obstacles can state we have to do all the good things in every time and place. Today, whether in the name of scientific egos of the people who put something in the name of humanity and be useful to the world that we think they've thought of that. Many thanks to the people who doing good things in the past, present and future, working to eliminate negativity on behalf of both today and future generations.

The domains
of our
research:

Cement Manufacturing

HTL Wels - Austria

The History of Cement Industry ¹

The use of mortar and cement dates back to the ancient Egypt and Mesopotamia. They used mud from the Rivers to join their unburned bricks. The Sumerians used clay, the early Babylonians employed bitumen. The Egyptian stone buildings were mortared with burned gypsum.

The Greeks used the first time Lime with a small amount of sand as mortar.

The Romans changed the mixture of the mortar at an amount of 75 % of sand and 25 % of lime. They reached a very high strength of this mixture due to a very good mixing and ramming procedure.

It was also the Romans who used a cement of the silicate type for the first time. They found that certain volcanic materials, mixed with lime and sand, gave a very strong mortar which even would set under water. The most famous source of this volcanic tuff was from Pozzuoli near Naples. This place gave the mortar the name Pozzolano.

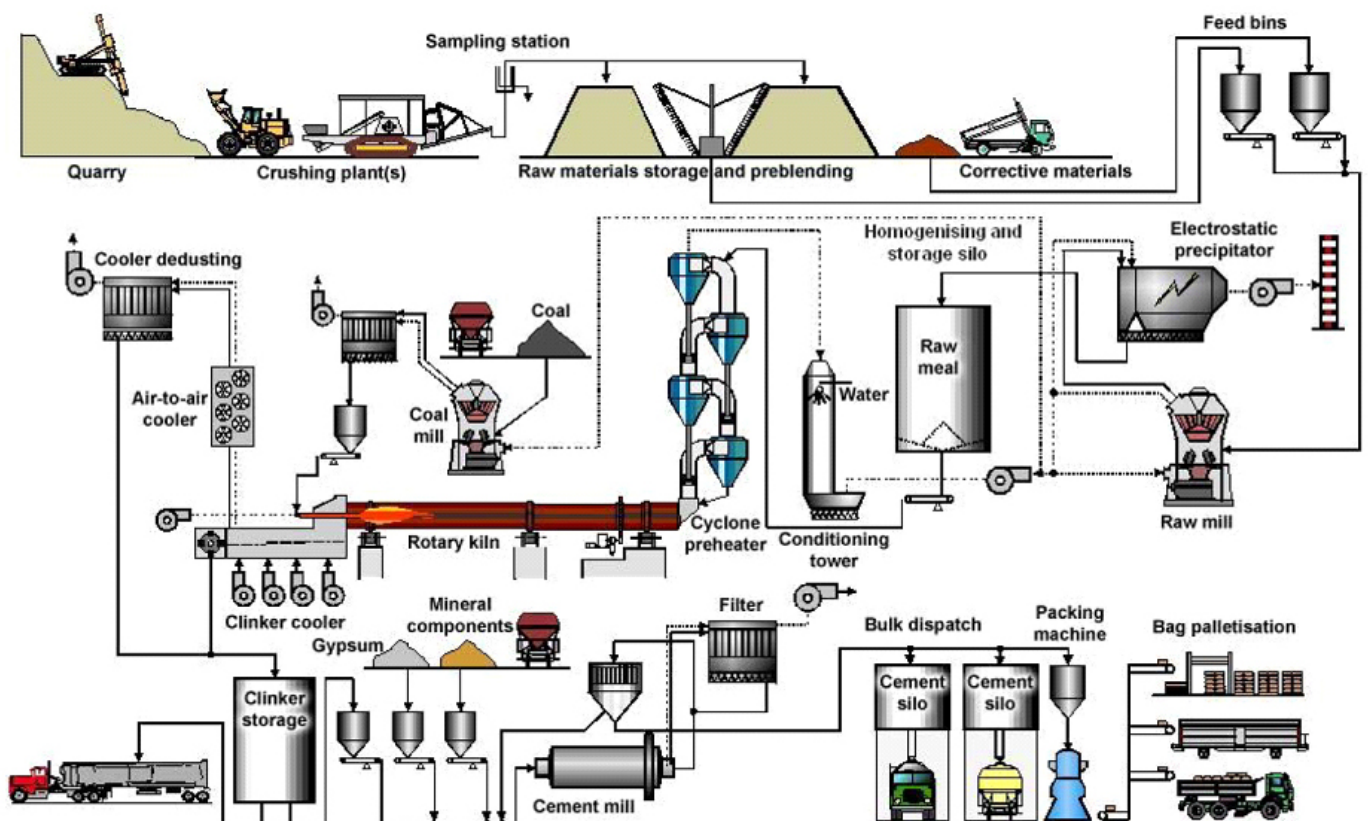
The buildings, built up at that periods are still standing (like the Aqueducts or the Colosseum).

In the middle ages the knowledge of this cement was forgotten. They used the mixture of lime and sand for the buildings again. But they also developed a mixture of lime and fine sand called attracum to be used similarly to cement .

The discovery of Portland Cement:

- **John Smeaton (1724-1792)** discovered the influence of lime and used the clayey limestone for the first time. He discovered hydraulic limestone
- **1824 Joseph Aspdin** was the first to patent Portland cement commercially used by his son William in 1848
- **1844 Isaac Charles Johnson** realized the impact of sintering -> Portland cement
French gardener Joseph Monier stabilized the concrete with a steel mesh
- **1870:** large scale production
- **1882:** Prüssing added blast furnace slag
- **1901:** Mix of blast furnace slag and cement clinker-> slag cement
- **1912:** concrete with high initial strength
- **1978:** steel fibre

Cement manufacturing process



Source: [103, CEMBUREAU, 2006]

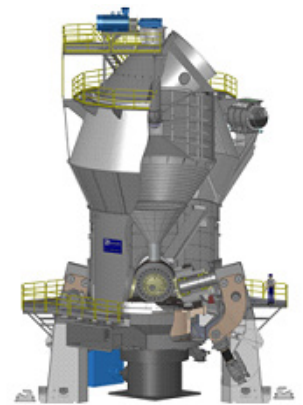
Extraction of the raw material

- **Mining**
- **Crushing of the rock**
- **Raw material mixture:** the different materials like limestone, clay, silicate and iron oxide are mixed according the planned product



Compilation of the mixture

- **Grinding in tumbling meals**
- **Homogeneous mixing** with external components to improve the property or to reduce the energy consumption like fly ash, blast furnace slag, silica fume, iron slag, paper sludge, pyrite ash, phosphogypsum (from flue gas desulphurisation and phosphoric acid production)



Burning process

- **Burning temperature:** up to 1450°C
- **Burning materials:** used oil, used tires, organic dump
- **The burning device** is a rotary kiln with a length up to 200m



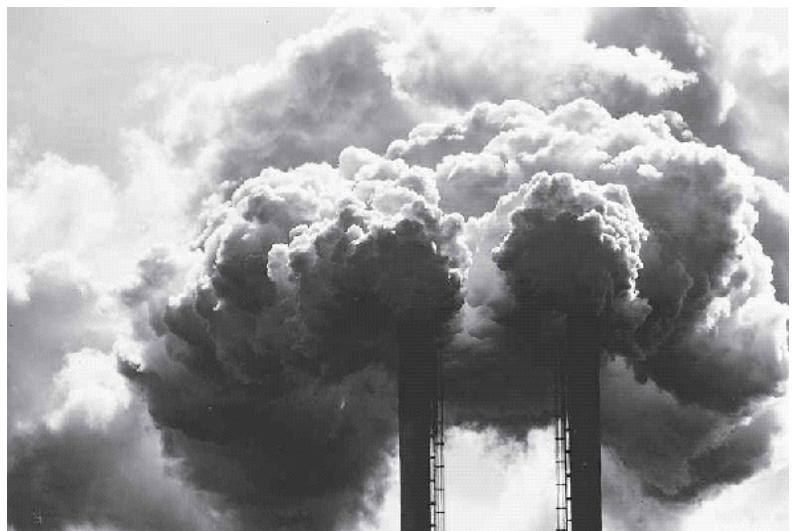
Additives, final product

- **granulated blast furnace slag**
- **gypsum**
- **lime**
- **ash**





- **Filtration of the exhaust gases** : Electrostatic precipitators for removal of dust.
- **SCR** -selective catalytic reduction or SNCR -selective non-catalytic reduction of NO_x
- **Recirculation of dust**





Organic Chemistry

Prof. gimnaziya po vet. medicina
"Ivan P. Pavlov" - Bulgaria

Organic chemistry is a big section of the chemical science studying the compounds of carbon, their structure, properties, methods of preparation, practical use. All compounds that contain carbon are called organic.

History of Organic Chemistry

Organic chemistry as a science did not exist until the middle of the XVIII century. At that time, it is divided into three types of chemistry: the chemistry of animals, vegetables and minerals.

In the first half of the 19th century it was proposed to separate the compounds of carbon in a separate chemical discipline - organic chemistry. Based on the accumulated extensive experience the first summaries were made defining the rapid development of the organic chemistry. Methods of analysis of organic compounds were developed, a theory of radicals is created, the concept of isomers was introduced .

In 1828 the German chemist F. Viller received urea. In 1854 the Frenchman Bertlo synthesized substances relating to the group of fat, and in 1861 Butlerov synthesized substances related to class Saccharides from formalin. These syntheses disproved the vital theory of inability to obtain organic compounds.

At the end of the 19th century the scientists have received all important representatives of hydrocarbons, alcohol, aldehydes and ketones, carboxylic acids, nitro derivatives, nitrogen and sulfur-containing heterocyclic structures.

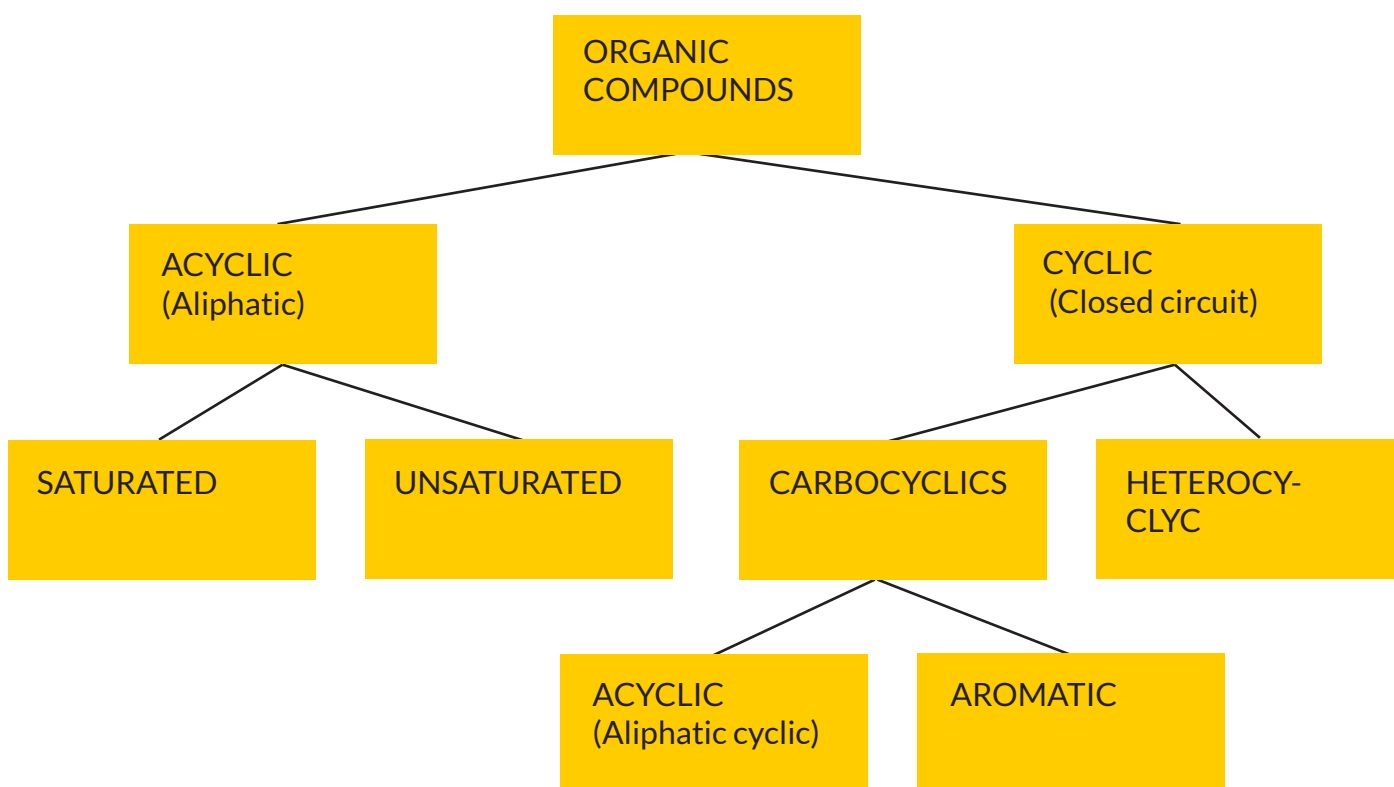
At the beginning of the 20th century by the methods of microanalysis of organic substances the chemistry of natural compounds has rapidly been developing: the scientist have determined the nature of the bile acids, cholesterol, porphyrin, bilirubin, heme, sex hormones, vitamin C, they have found new types of physiologically active compounds, complexone and others.

Due to the special properties of the carbon, organic substances are numerous and there are more than 91 million compounds, registered in the beginning of 2015, and their number is constantly growing according to the CAS - Chemical Abstracts service.

Diversity and the vast number of organic compounds determined importance of organic chemistry as the largest share of the modern chemistry. The world around us is mainly composed of organic compounds: food, clothes, medicines, detergents, paints, dyes, etc. They play an important role in people's lives.

Organic compounds can be classified according to:

1. The structure of the carbon chain:



2. Classification of the organic compounds depending on the functional group:

1. HYDROCARBONS- (H)
2. Halocarbon (Hal)
3. Alcohol (OH)
4. ALDEHYDES (COH)
5. ACID (COOH)
6. AMINES (NH₂)
7. Nitro (NO₂)

The role of organic compounds in our lives

1. Organic chemistry around us

The lower part of the substances is not organic in nature and most of them are organic. Every person and animal synthesizes organic molecules every second. For example, living organisms are composed of proteins which are made up of amino acids, which are the simplest organic compounds. We face polymers daily, which are synthesized from organic compounds - monomers.

2. Development of drugs

The most important field of the organic chemistry nowadays is the search and synthesis of new medicines in human and veterinary medicine.

3. Organic chemistry in agriculture

Many of the products used in agro chemistry are piretrids to combat insects, fungicides - antifungal agents, etc.

4. Organic chemistry in the veterinary medicine- veterinary antiparasitic drugs:

Disinfectants, anti-insects detergents, alcohol, muscle relaxants, tranquilizers, cardiovascular agents, antispasmodics, vitamins and others.



The use of alternative solvents

Chemical reactions are varied and they are carried out in a wide range of pressure and temperature. Reactions were secured by these three components:

- Solvent
- Reagent / a catalyst
- Use of energy

Scientists are developing a lot of rational synthetic processes corresponding to green chemistry. These methods allow reducing waste, the loss of energy, flammable solvents. At the heart of the green chemistry alternative solvents are applied. The most famous environmental reactions are:

- **The use of safe solvents**
- **Water as a solvent**
- **Reactions without a solvent**
- **Supercritical water (3740 C, n218 atm.)**
- **Ionic liquids**

Many of the traditional solvents are volatile organic compounds, poisonous substances polluting the air. They can harm seriously person's health. The used solvents (benzene, chlorine organic compounds,) are very often famous for their carcinogenicity.

The safest solvents include - **amyl alcohol; 2-butanol; butyl acetate; ethyl acetate** and the like. They are known as “*green solvents*”, environmentally friendly, which occur in the processing of cereals. For example, ethyl lactate solvent is obtained by the processing of grain. It can replace such solvents as toluene, acetone and xylene.

The use of water as a solvent - all biochemical processes in the organisms are carried out in an aqueous environment.

Reactions without a solvent

The advantages of the solvent-free reactions are:

- the absence of intermediate reactions and substances which need to be purified and destroyed
- pure compounds are formed, which do not need a treatment - chromatography
- reactions are made faster
- less energy consumption

Biocatalysis - it is the green chemistry.

The inclusion of bio catalysis in the chemical industry in recent years is accelerated thanks to the development of microbiology and biotechnology. By forecasts in recent years up to 20% of the production of industrial chemicals will be due to the biotechnologies. The use of enzymes and microorganisms is the perfect choice for “*green*” chemistry. They are standard reactions between organic substances catalysed by them. Microorganisms have the ability to grow rapidly and to adapt to the new environment. These features enable their large-scale cultivation without major losses.

Today scientists are successfully developing new methods such as extractive biocatalysis, immobilization, biocatalysis in organic solvents and technology for recombination of DNA for production of enzymes. Production of proteins and cell cultures and the fusion of cells will become useful methods for microbiological synthesis in the near future. A large amount of biological and useful chemical compounds are obtained using microorganisms. Bacterial enrichment of the soil is a method of microbiology. Enzymes are used in the production of detergents and new antibiotics. There are bacteria, which can exist at high and at low temperatures. The method of purification of soil and water, using the help of such bacteria, is the most profitable.

Examples of application of the fermentation:

- **Receiving glucose-fructose syrup from starch:** Three fermentation are used - amylase, glucoamylase and glyukoizomeraza;
- **Processing of milk plasma:** The ferment is a beta-galactosidase, splitting of the milk sugar in lactose and glucose. This method is for the treatment of milk and the producing of lactose-free milk;
- **Production of ethanol, beer:** the enzymes are used for the preparation of glucose-fructose syrup;
- **The processing of milk into cheese and cottage cheese** - milk clotting ferment;
In the production of wine and juices - it is used the ferment pectinase for preparing a soluble sugar;
- **Preparation of L-amino acids by D-amino acids**, which are obtained by chemical synthesis. This isomerization is carried out by the ferme aminoacylase;
- **Conversion of steroids** (the hydrocortisone to prednisolone) is carried out by the ferment dehydrogenase.

Pharmaceutical Industry

Petrik Lajos Bilingual Vocational School of Chemistry - Hungary



The use of medicinal substances dates back to the prehistoric era. Every form of the early cures arrived directly from natural sources¹. In order to follow this line, our group studied vitamins and other nutrients via the study of natural **vitamin C**^{2,3} sources and the investigation of the iron content of food⁴. Our studies proved their availability in nature, and also emphasised the limited amount of the effective agents present in them in spite of the modern medicinal trends and beliefs. Our findings revealed the importance of synthetic methods to produce effective substances.

As pharmaceutical science studied a wide range of areas, the scope of the Hungarian project duties was paved by the development of a pharmaceutical version of the timeline game to point out the most important effective substances. The laboratory practices for the study of some medicinal chemicals were exploited to the highest extent concerning our ways and means.

During the study of **disinfectants**, TCP (trichlorophenol) was produced with the direct chlorination of phenol at semi-micro scale⁵. The necessary substances (bleach with sodium hypochlorite effective agent, concentrated hydrochloric acid and phenol) underwent a thorough examination to learn about their properties and careful use and storage. Further efforts were put into the fine of dangers and emergencies such a synthesis method at industrial scale may impose.

Nowadays TCP-based disinfectants are not commonly used, their use is restricted to some specific areas (e.g. in sterile soaps for areas destroyed by natural disasters). However there are still common medical procedures that use phenolates (surgical treatment of ingrown toenails).

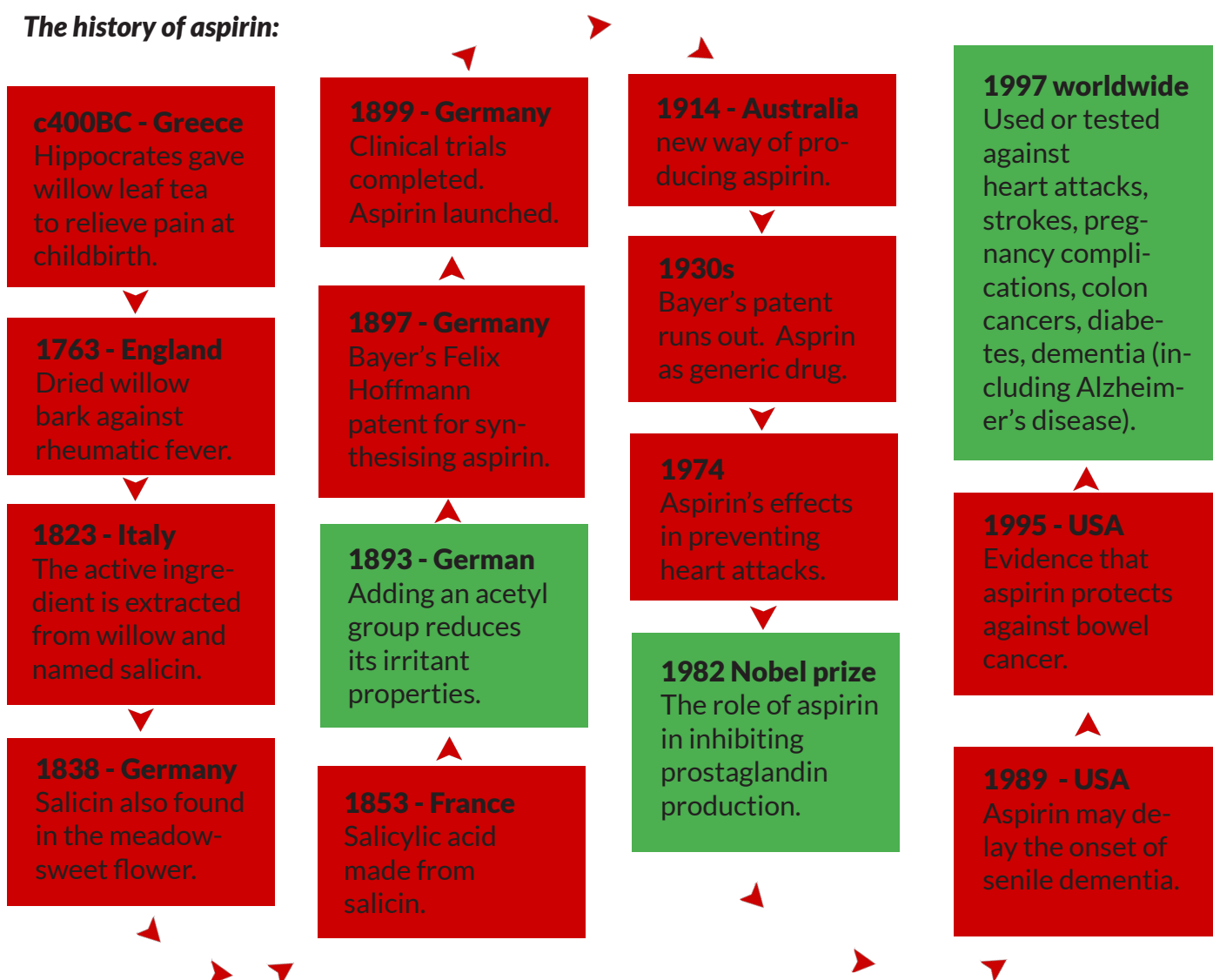
The following conclusion was drawn: the effective substances of pharmaceutical products are not safe and secure white powders, since the required effect must be reached.

The majority of work was done in the field of analgesics⁶. **Analgesics** are split into three main families of pain-killers, out of which aspirin from the carboxylate or salicylate family was detailed due to the typical laboratorial synthesis method from salicylic acid.

The pharmaceutical industry of the 19th and the 20th century is characterised by the spread of synthetic effective agents. An important milestone was the discovery of the Kolbe synthesis, which produced **aspirin** in six steps starting from the benzene content of crude oil. Our lab work examined the last step with our newly developed and wide-opened green eyes. These days aspirin⁷, and its counterpart Kalmopyrin patented by Richter, the Hungarian pharmaceutical company are less popular. According to available statistics the lead has been taken by **ibuprofen**. This change is partially made by the green make-over of the industry⁸.

The effective substance of aspirin also found **a green synthesis** for the fulfilment of its new carrier requirements as several studied of the 20th century pointed out its efficiency in new areas (**Aspirin Protect**, a supportive and preventive pill for the heart). At lab scale our study included microwave production method⁹ and the manufacture of aspirin capsules.

The history of aspirin:



The history of pharmaceuticals is double-faced: many of the severe and formerly fatal diseases were taken under control or globally eradicated, meanwhile the dangers which lurked in the complexity of effective structures turned into tragedies and scandals (e.g. Contergan scandal of the 60's and other side-effects).

The industrial disasters linked to chemical industry were placed outside of the realm of pharmaceuticals, the impact was shared. The bad reputation inherited due to the disasters found some suitable roots in the characteristics of pharmaceutical industry by 1980s including profit orientation, huge amount of waste, air pollution and waste of energy. Many steps were taken in order to lessen these problems (as eradication is not a real-life alternative) and led to sweeping changes:

- **Numerous legislative steps**
- **Severe legal control**
- **Reduction of waste**
- **Spare of energy**
- **Recycling**

These changes resulted in the fundamental transformation of the industry, as the manufacture of 1 ton pharmaceutical product may produce 100 tons of waste. Several theoretical studies aimed to decrease the environmental factor are in progress. The everyday operation of the companies was affected at all levels by the ban of some solvents and the reduction in the use of organic solvents. The dream of solvent-free pharmaceutical industry cannot be put into practice in accordance with present scientific development.



Hungarian pharmaceutical companies can exhibit some promising new methods:

- The pharmaceutical company **Sanofi** invented a technology of lower water demand;
- The regeneration of many solvents is successful making **58% of the solvents recycled**.
- A few chemical free **cleaning technologies** are also in use.
- **EGIS** Company uses an innovative formulation technology for its product Ketilept which avoids organic solvents.

For the sake of clarity, one must be aware of how requirements and demand changed over the years. The old effective agents (salicylates, penicillin) caused allergy in far more patients than the situation could be handled. The sensitivity to medications made their replacement necessary. Penicillin was replaced by wide-spectrum antibiotics; however it kept its position as the efficient cure of syphilis without any equal substitute.

The production of new effective agents is led by low-risk of side effects and catalysis. In one hand selective catalysts are very important in pharmaceutical industry due to the alternative pathways of producing a given substance with lower energy demand and fewer auxiliaries accompanied by the reduction of waste. It is one of the main fields of interest: production routes may include fewer steps with their help. In the case of ibuprofen 6 steps were cut to 3. On the other hand these catalysts are absolutely high expenses and require regain and regeneration studies.



The modern pharmaceutical industry appears very futuristic with:

- *Constant monitoring and real-time analysis*
- *High level of computerisation*
- *Millions of euro investments into eco efficiency*
- *High level of social and community involvement*



Water Quality and Supplies

ITIS Pininfarina - Italy

Water, H_2O , is an amazing chemical compound. It is the true medium of life. Early life forms developed in water and only much later in their evolution ventured out of water, but never very far. Our own bodies are largely water. Our blood is a water solution of sodium chloride and other essential salts, in which are suspended colloidal-sized red blood cells that carry oxygen from the lungs throughout the body. Even those organisms that dare to live in water-deficient areas — camels, gila monsters, cactus, and some poorly washed humans — must have elaborate mechanisms to conserve, store, and obtain the small quantities of water in their surroundings.

Water has several important properties that are of crucial importance for its role as a solvent, life medium, environmental behavior, and industrial uses, based upon the following characteristics of the water molecule:

- ***Unsymmetrical molecule***
- ***Polar nature of the water molecule***
- ***Ability to form hydrogen bonds***

Water is an excellent solvent for a number of materials, including salts, acids, bases, and substances that have H, O, and N atoms capable of forming hydrogen bonds. As a result, water is the solvent in biological fluids, such as blood or urine; it acts to weather minerals and transport dissolved minerals in the geosphere; it transports nutrients to plant roots in soil; and it has many industrial uses.

Water has a very high surface tension and liquid water, such as that in rain droplets, behaves physically like it is covered with a thin membrane. Ducks appreciate this characteristic of water because it enables them to float on a water surface. A duck will sink in water to which a detergent has been added to lower the surface tension, which the birds find to be very distressing. Water is transparent to visible light and to the longer-wavelength fraction of ultraviolet radiation. This enables photosynthesis to occur in algae suspended under the surface of water.

Even more so than energy, the availability of affordable water will determine the development of civilization in future decades. Much of the world suffers from a chronic shortage of water.

To prevent water pollution, effective safety measures should be employed that prevent point-source and nonpoint-source pollution. Green chemistry solutions should be employed, where possible. An effective way to deal with the water pollution problem is to use the least harmful ways to eliminate contaminants.

Most experts agree that water will be the next major environmental stress issue, rivaling and perhaps exceeding global climate change for technical and management solutions in the coming decades. The source of the water crisis is simple but exceedingly difficult to address, water resources are finite and the population that depends on those supplies is increasing inexorably. Virtually all of the global environmental impacts attributable to this population growth have ties to or severe impacts on water resources:

- **Deforestation resulting from the demand for agricultural land**, housing, and fuel
- **Loss of biological species in forests and in waters**
- **Desertification, erosion, and salination of farmland** from unsustainable agricultural practices
- **Pollution of fresh and marine waters**, further depleting food sources
- **Introduction of persistent organic pollutants into the ecosystem**
- **Changing climate** with as yet unpredictable changes in the hydrologic cycle having \ manifestations in flood, drought, sea-level change, and the spread of infectious diseases

Among water issues facing the world today, land-based sources of water pollution are among the most pressing. Adequate supplies of satisfactory-quality water are essential for the natural resources and ecological systems on which all life depends. An estimated 20 % of the world's freshwater fish and 80% of estuarine-dependent fish species, for example, have been pushed to the brink of extinction by contaminated water and loss of or damage to their habitat.

Addressing sustainability issues such as water and food production cannot be a choice between resources or the environment. Instead, there have to be more innovative solutions. Fundamentally, water quality is going to have to be tackled along with water quantity.

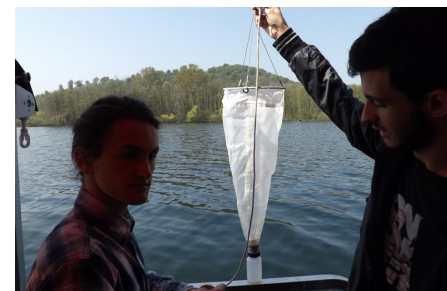
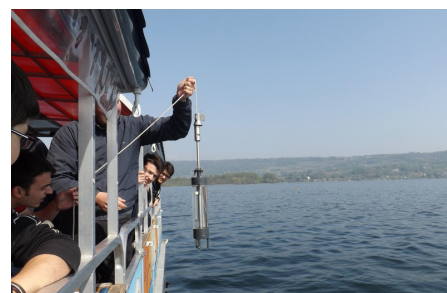
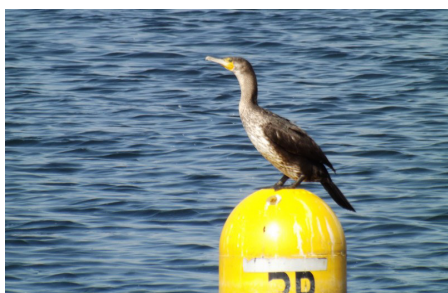
For example, 70% of the water in China is contaminated and unusable for human consumption. This is typical of many developing countries. A lot of contamination is human waste. That can certainly be managed with infrastructure: collection and treatment. However, there is also a lot of industrial waste containing persistent metals and organics that must be avoided from the beginning. Water quantity will not be dramatically increased so water quality must be addressed.

Part of the answer for developing countries therefore is to be able to reuse water repeatedly. Green chemistry is really a viable approach to such global environmental problems. Solutions may come on a process-by-process basis.

Green chemistry offers a scientifically based set of solutions for protecting water quality and is a viable approach to global environmental problems. However, success requires an effective and complex blend of technical, social, economic, and political contributions.

Of the 12 principles of green chemistry, these can be directly applied to solving water pollution problems:

- **Minimize waste:** Ideally, no waste should remain that requires treatment or cleanup.
- **Use catalysts:** Use catalytic rather than stoichiometric reactions that use excess reagents, and work only once.
- **Use safe solvents:** Avoid using unsafe solvents, separation agents, or other auxiliary chemicals. Use innocuous chemicals if it is necessary.
- **Increase energy efficiency:** Run chemical reactions at ambient temperatures and pressures, when possible.
- **Design chemicals and products that degrade after use:** To prevent accumulation in the environment, design chemical products to break down to innocuous substances after use.
- **Analyze in real time:** Include in-process, real-time monitoring and control during syntheses to minimize or eliminate the formation of by-products.



Lab activity on Viverone lake

On 16th April 2015, our students spent their educational activity in projects and experiments concerning our project domain, WATER. They spent one day on Viverone Lake, making analysis of the lake water, the possible pollution agents and reactions. Here are the pictures of their activity.

Green chemistry examples:



Photographic Chemicals

Several heavy metals are among the more troublesome water pollutants, with a number of others in more isolated cases. Obviously, it is important to prevent such elements from getting into water. Here the practice of green chemistry plays an important role. One approach is to strictly forbid the release of heavy metals into water. This has worked reasonably well but, as with all command and control measures, it is subject to human oversight, accident, and even deliberate releases made to try to avoid disposal costs.

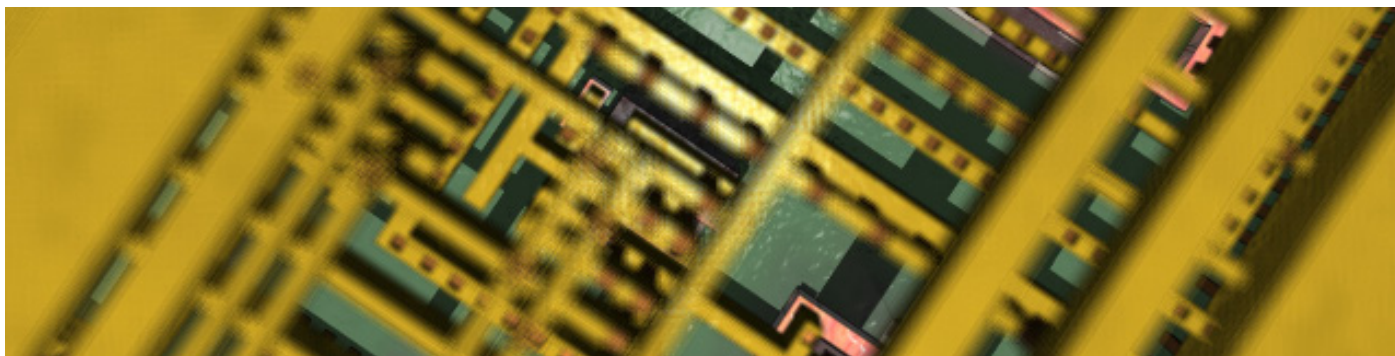
A much better approach, where possible, is to use the principles of green chemistry to avoid any possibility of pollutant release.

Moreover, Life-Cycle Analysis (LCA), a tool of green chemistry, is a way of examining the total environmental impact of a product through every step of its life—from obtaining raw materials, through making the product in a factory, selling it in a store, using it in the home, and disposing of it. LCA reveals true waste costs. Companies have wasted a lot of money over the years on waste disposal and waste treatment. In looking at these costs, it makes sense that companies began to realize very quickly that control over process efficiency was also a control over cost. Decreasing pollution fundamentally increased profit, so movement into this area happened quickly.

The ways in which water sources become contaminated are sometimes surprising. **Photographic processing**, for example, is one of the great “out-of-sight, out-of-mind” sources of water contamination. People across the world send their photographs out for processing each day, quite unaware of the major source of contamination that comes from photographic chemical developer simply dumped down drains.

DuPont has come up with a new photographic development system called **DuCare™** that addresses this waste issue. With the DuCare system, hydroquinone developer is replaced with erythorbic acid, and 99% of the developer and fixer is recycled at a central facility. The chemicals are actually distributed in containers that once used are returned to DuPont for recycling. Thus, not only is the chemistry of the developer replaced, the way in which the photographic chemicals are distributed is as well. Overall, DuPont changed the nature of the business. Instead of just being a chemical supplier, it now provides a valuable service. DuPont came up with a way of delivering fixers and developers to stores that enables elimination of water use and contamination and is great for its bottom line. The only water involved now is what is originally put in the DuPont photographic processing system.

Semiconductor Manufacturing



This example involves **semiconductor fabrication**. Water is really a huge issue here. For example, in the US, the average semiconductor fabrication plant will go through 2 million to 3 million gallons of deionized water a day. Typically the plants are located in semiarid regions of the country (e.g., Austin, TX; Albuquerque, NM; San Jose, CA; and Irvine, CA) that already struggle with water issues. Then it was found that supercritical fluids, especially supercritical CO₂, could be used for cleaning instead of water. This is because in the supercritical state, CO₂ has no surface tension and can penetrate the small spaces with the addition of propylene carbonate, a food additive. This technology has been commercialized, and the supercritical fluid technology has won a Presidential Green Chemistry Challenge Award.

Marine Environment - Antifoulants

Every ship has the problem of buildup of marine organisms. **Organisms on ships' surfaces** increase drag and fuel costs, but cleaning them off is an expensive process, and takes a ship out of service. The typical approach to this problem has been the use of tributyltin in paint. Tributyltin kills marine organisms, but unfortunately, it also bioaccumulates and becomes toxic to larger organisms.

In coastal regions, immune, reproductive, and mutagenic effects in marine organisms are now quite high. This makes less food available in coastal regions and has led to some very long term impacts.

Rohm and Haas looked at this problem and developed the new **Sea-Nine® antifoulant**, 4,5-dichloro-2-n-octyl-4- isothiazolin-3-one (DCOI). The metabolic breakdown products of DCOI are nontoxic and do not bioaccumulate. DCOI is also cost competitive with tributyltin. It thus made sense for ship-owners to switch to the less toxic alternative. Adoption of the new antifoulant was also facilitated by the number of international regulations beginning to ban the use of tributyltin. Again, regulation coupled with effective chemistry tools has helped ship-owners move to use of the more environmentally friendly alternative and eliminate the use of tributyltin.

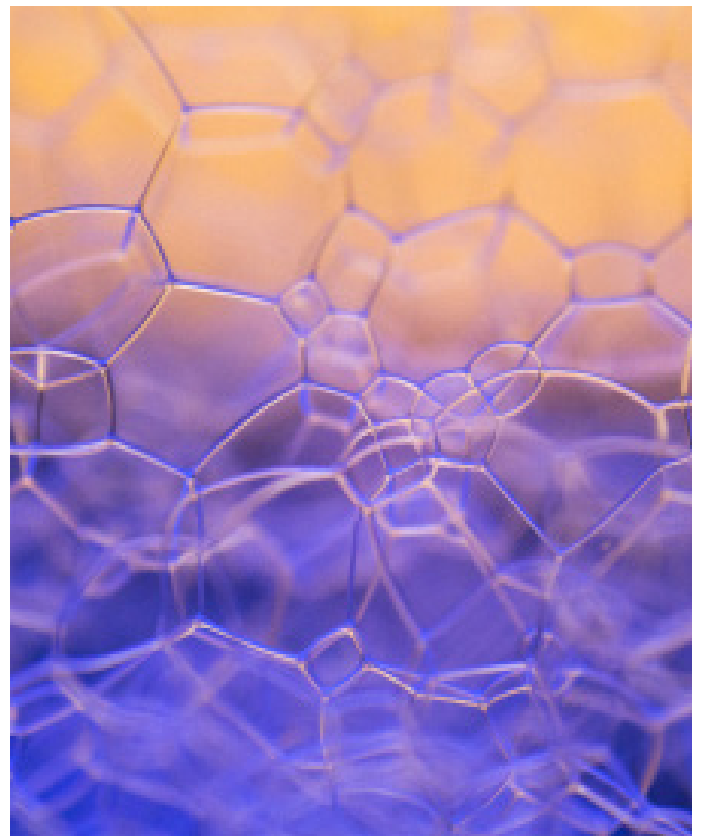
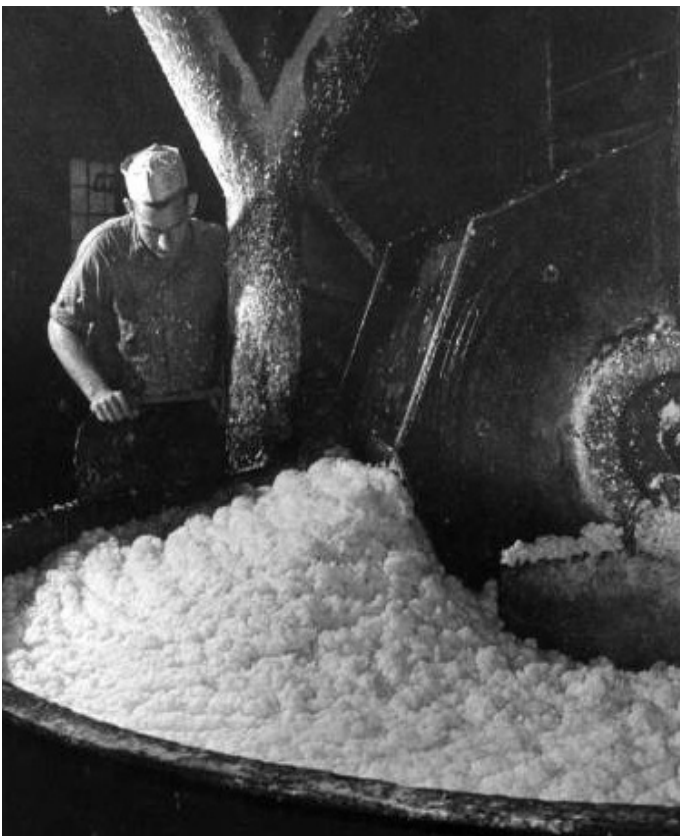


Pulp and Paper Processing

The bleaching of pulp depends on *the systematic separation of lignin from cellulose*. The chemical processes of the pulp and paper industry are primarily directed to separating these two components. In nature, the biodegradation process accomplishes this using a limited suite of enzymes: ligninase, glyoxal oxidase, and Mn peroxidase. To achieve the same oxidation for which nature uses O_2 , industry has substituted chlorine compounds, resulting in the release of phenolic compounds and environmentally persistent organochlorine compounds.

Dr. Terry Collins at Carnegie-Mellon University has developed oxidant activators derived from iron called tetraamido-macrocyclic ligands (**TAML™**). When combined with hydrogen peroxide in water, the TAML activators produce a reaction equivalent to oxidizing enzymes in nature.

Craig Hill (Emory University) and Ira Weinstock (**USDA**) developed a catalytic approach designed to mimic the processes of nature. The process utilizes nontoxic and inexpensive organic compounds called *polyoxometalates*. First, the lignin is removed from the wood pulp through oxidation with polyoxometalates. Then, O_2 is added to the bleaching liquor and the same poly-oxometalate catalyzes the mineralization of the dissolved lignin fragments. The result is an effluent-free process.



Detergents

The earliest developed synthetic detergents were non-biodegradable due to their branched hydrocarbon chains. It was discovered that they did not decompose within a few days and thus persisted in the environment. These caused waterways in the 1960s and 70s to build up with foam. Industrial chemists eventually rectified this problem by *synthesizing detergents with non-branching tails* which are more easily broken down by microbial decomposers.

Cosmetic Field

Ana Aslan Technical
College - Romania



Ana Aslan Technical College is a Vocational Secondary School situated in Cluj Napoca, the largest city in Transylvania and the economic and cultural capital of this region.

Our role in the project was to make the research of the 12 principles of Green Chemistry in the cosmetic domain, working on the booklet and the curriculum of local development and to organize the final project meeting with Farmec S.A.



We invited Farmec S.A. Company, one of the most prestigious cosmetic companies in Romania to be involved as true Partner in our Project. Our school has very good relations with this Company where our pupils make their practical work.

The correlation between the theoretical knowledge and the industrial reality, benefit from the skills of an industrial partner (Farmec S.A.) and the scientific specialty consultancy provided by university professors from the Faculty of Chemistry and Chemical Engineering from Babes-Bolyai University of Cluj-Napoca, Romania.

During the project, our team made researches on the 12 principles of Green Chemistry applied in Farmec Company from Cluj-Napoca, Romania. Most of them will be used to obtain professional certificates by our students when they have finished high school.



The cosmetic industry worldwide is developing continuously, now more than ever. The cosmetic industry is a fascinating and a provocative domain.

A cosmetic product is a substance or a mixture of substances intended to be placed in contact with the external parts of the human body (epidermis, hair system, nails, lips and external genital organs) or with the teeth and the mucous membranes of the oral cavity with a view exclusively or mainly to cleaning them, perfuming them, changing their appearance, protecting them, keeping them in good condition or correcting body odours.

Cosmetics include skin care products (creams, emulsions, lotions, serums, gels, soaps), hair care products (shampoos, sprays, gels, serums, masks and conditioners), oral care products (tooth paste, mouthwash), perfuming products (perfumes, body sprays, antiperspirans, deodorants) and make-up products (mascaras, lipsticks) and nail products (nailpolishes, nailpolish removers, lotions).

Cosmetics were used since ancient times by Egyptians, Greeks and Romans. The Egyptians used castor oil as a protective balm and the Romans used skin creams made of beeswax, olive oil and rosewater.

First of all when you formulate a cosmetic product you must comply with the legislation. You have to use only the cosmetic ingredients that are allowed to be used. There are substances that are prohibited to be used in cosmetic products and there are substances that may be used until to a maximum concentration depending the type of the product.

For having a safe product and for reaching performance, a lot of tests must be performed: the stability tests of the formulation, the compatibility tests between the formulation and the packaging, the Challenge tests, the dermatological tests, the safety assessments and different efficacy tests.

The care for beauty and the respect towards tradition, health and environment, completed by the continuous research, originality and attention for the needs of population, have turned the cosmetic companies to develop different formulations, for different types of problems.

Continuously changing of the cosmetic products is due to several reasons: updating and innovation of new cosmetics ingredients, new lifestyles, new different habits, new trends in fashion etc.

The cosmetic industry is important, because everybody wants to feel and wants to be more beautiful.

Green chemistry in cosmetics means:

- **Eco friendly technologies in order to obtain the raw materials** (using biocatalytic processes, eliminating the use of organic solvents, processes generating minimal amounts of waste).
- **Using raw materials from renewable resources** in order to ensure sustainability and a sustainable development.
- **Achieving the manufacturing of finished goods using environmentally friendly ingredients** and which are safe for human health at the same time.

The application steps of green chemistry principles within FARMEC:

The **Farmec Company** applied the principles of green chemistry throughout its whole development as follows:

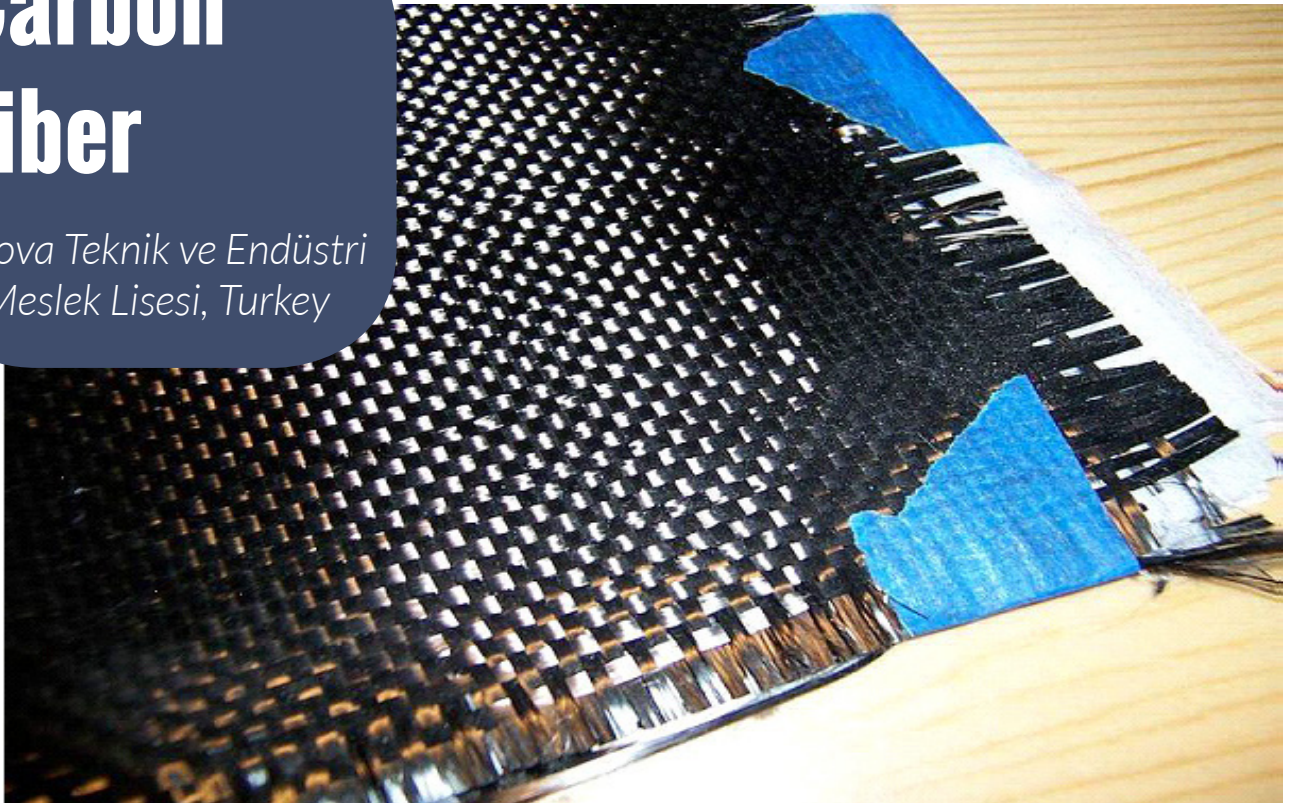
- In 1985 it manufactures the cosmetic line GEROVITAL-Plant where synthetic active ingredients are replaced by **active ingredients of plant origin**.
- In 1995 is inaugurated the new factory (the only one in Romania) to manufacture **CFC-free aerosol based products** (CFCs/the chlorofluorocarbons being a major cause contributing to ozone depletion).



- In 1998 petrochemically derived mineral oils are replaced by **vegetable oils**.
- In 2000 the cosmetic line ASLAVITAL is launched, for which the active ingredient is a **natural clay** from Romania with no chemical treatment.
- In 2002 are introduced in the production line the first creams obtained through a **cold process technology** in order to reduce energy consumption: the AVER line.
- In 2003 we start **exclusive use of vegetable origin glycerin**, coming from renewable resources.
- Starting 2005 **only biodegradable surfactants** are being used in our products.
- In 2007 a new department of the production site is launched which is fully compliant with **GMP** (Good Manufacture Practices) technologically and environmental safety, using modern equipment, of high capacity, to fulfill the safety conditions of our products, the environmental safety and to reduce energy consumption .
- In 2008 it starts the **replacing of parabens** from our formulations. We have nowadays a few products with these preservatives with a possible risk on human toxicity.
- In 2009 is launched the modernized line **GEROVITAL Plant**, not only paraben-free, but preservative-free as well, with organic Edelweiss Extract, eco-certified.
- In 2011 FARMEC complies with the **ISO 14001/2004 Environmental Management** System, ensuring the framework to apply all principles for a sustainable development, to prevent pollution, a well-balanced waste management and a continuous improvement of environmental performance.
- In 2012 the product NUFAR is launched – a descaler, first product on Romanian market that uses **fully biodegradable methanesulfonic acid**.
- In 2013 is launched the cleaning products range NUFAR Verde (Green) based on natural ingredients, biodegradable surfactants, containing chamomile eco-certified extract, packaged in **recyclable packaging**.

Carbon Fiber

Yalova Teknik ve Endüstri
Meslek Lisesi, Turkey



Carbon fiber, alternatively **graphite fiber** or **CF**, is a material consisting of fibers about 5–10µm in diameter and composed mostly of carbon atoms.

To produce carbon fiber, the carbon atoms are bonded together in crystals that are more or less aligned parallel to the long axis of the fiber as the crystal alignment gives the fiber high strength-to-volume ratio (making it strong for its size). Several thousand carbon fibers are bundled together to form a tow, which may be used by itself or woven into a fabric.

The properties of carbon fibers, such as high stiffness, high tensile strength, low weight, high chemical resistance, high temperature tolerance and low thermal expansion, make them very popular in aerospace, civil engineering, military, and motorsports, along with other competition sports. However, they are relatively expensive when compared to similar fibers, such as glass fibers or plastic fibers.

Carbon fibers are usually combined with other materials to form a composite. When combined with a plastic resin and wound or molded it forms carbon-fiber-reinforced polymer (often referred to as carbon fiber) which has a very high strength-to-weight ratio, and is extremely rigid although somewhat brittle. However, carbon fibers are also composited with other materials, such as with graphite to form carbon-carbon composites, which have a very high heat tolerance.

History

In 1879, Thomas Edison baked cotton threads or bamboo slivers at high temperatures carbonizing them into an all-carbon fiber filament used in the first incandescent light bulb to be heated by electricity.¹ In 1880, Lewis Latimer developed a reliable carbon wire filament for the incandescent light bulb, heated by electricity.²

In 1958, Roger Bacon created high-performance carbon fibers at the Union Carbide Parma Technical Center, now GrafTech International Holdings, Inc., located outside of Cleveland,

Ohio.³ Those fibers were manufactured by heating strands of rayon until they carbonized. This process proved to be inefficient, as the resulting fibers contained only about 20% carbon and had low strength and stiffness properties. In the early 1960s, a process was developed by Dr. Akio Shindo at the Agency of Industrial Science and Technology of Japan, using polyacrylonitrile (PAN) as a raw material. This had produced a carbon fiber that contained about 55% carbon.

The high potential strength of carbon fiber was realized in 1963 in a process developed by W. Watt, L. N. Phillips, and W. Johnson at the Royal Aircraft Establishment at Farnborough, Hampshire. The process was patented by the UK Ministry of Defence, then licensed by the NRDC to three British companies: Rolls-Royce already making carbon fiber, Morganite, and Courtaulds. Within a few years, after successful use in 1968 of a Hyfil carbon-fibre fan assembly in the Conways of the Vickers VC10s operated by BOAC⁴, Rolls-Royce took advantage of the new material's properties to break into the American market with its RB-211 aero-engine with carbon-fiber compressor blades. Unfortunately, the blades proved vulnerable to damage from bird impact. This problem and others caused Rolls-Royce such setbacks that the company was nationalized in 1971. The carbon-fiber production plant was sold off to form "Bristol Composites".

In the late 1960s, the Japanese took the lead in manufacturing PAN-based carbon fibers. The 1970 joint technology agreement allowed Union Carbide to manufacture the Japan's Toray Industries superior product and USA to dominate the market. Morganite decided that carbon-fiber production was peripheral to its core business, leaving Courtaulds as the only big UK manufacturer. Continuing collaboration with the staff at Farnborough proved helpful in the quest for higher quality and improvements in the speed of production as Courtaulds developed two main markets: aerospace and sports equipment. However Courtaulds's big advantage as manufacturer of the "Courtelle" precursor now became a weakness. Courtelle's low cost and ready availability were potential advantages, but the water-based inorganic process used to produce it made the product susceptible to impurities that did not affect the organic process used by other carbon-fiber manufacturers.

Nevertheless, during the 1980s Courtaulds continued to be a major supplier of carbon fiber for the sports-goods market, with Mitsubishi its main customer until a move to expand, including building a production plant in California, turned out badly. The investment did not generate the anticipated returns, leading to a decision to pull out of the area and Courtaulds ceased carbon-fiber production in 1991. Ironically the one surviving UK carbon-fiber manufacturer continued to thrive making fiber based on Courtaulds's precursor. Inverness-based RK Carbon Fibres Ltd concentrated on producing carbon fiber for industrial applications, removing the need to compete at the quality levels reached by overseas manufacturers.

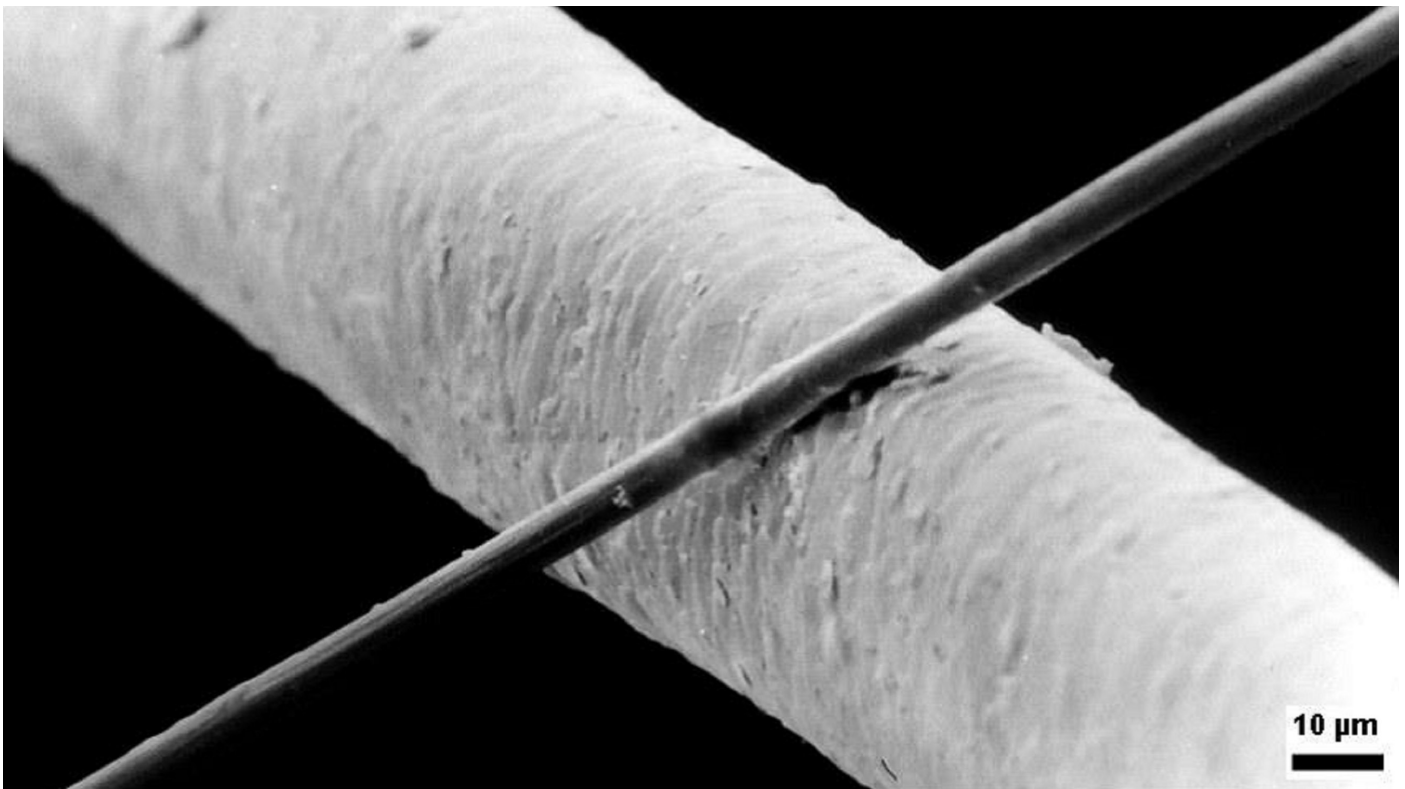
During the 1960s, experimental work to find alternative raw materials led to the introduction of carbon fibers made from a petroleum pitch derived from oil processing. These fibers contained about 85% carbon and had excellent flexural strength. Also, during this period, the Japanese Government heavily supported carbon fiber development at home and several Japanese companies such as Toray, Nippon Carbon, Toho Rayon and Mitsubishi started their own development and production. As they subsequently advanced to become market leaders, companies in USA and Europe were encouraged to take up these activities as well, either through their own developments or contractual acquisition of carbon fiber knowledge. These companies included Hercules, BASF and Celanese USA and Akzo in Europe.

Since the late 1970s, further types of carbon fiber yarn entered the global market, offering higher tensile strength and higher elastic modulus. For example, T400 from Toray with a tensile strength of 4,000 MPa and M40, a modulus of 400 GPa. Intermediate carbon fibers, such as IM 600 from Toho Rayon with up to 6,000 MPa were developed. Carbon fibers from Toray, Celanese and Akzo found their way to aerospace application from secondary to primary parts first in military and later in civil aircraft as in McDonnell Douglas, Boeing and Airbus planes. By 2000 the industrial applications for highly sophisticated machine parts in middle Europe was becoming more important.

Structure and properties

Carbon fiber is frequently supplied in the form of a continuous tow wound onto a reel. The tow is a bundle of thousands of continuous individual carbon filaments held together and protected by an organic coating, or size, such as polyethylene oxide (PEO) or polyvinyl alcohol (PVA). The tow can be conveniently unwound from the reel for use. Each carbon filament in the tow is a continuous cylinder with a diameter of 5–8 micrometers and consists almost exclusively of carbon. The earliest generation (e.g. T300, HTA and AS4) had diameters of 16–22 micrometers.⁵ Later fibers (e.g. IM6 or IM600) have diameters that are approximately 5 micrometers⁵.

The atomic structure of carbon fiber is similar to that of graphite, consisting of sheets of carbon atoms arranged in a regular hexagonal pattern (graphene sheets), the difference being in the way these sheets interlock. Graphite is a crystalline material in which the sheets are stacked parallel to one another in regular fashion. The intermolecular forces between the sheets are relatively weak Van der Waals forces, giving graphite its soft and brittle characteristics.



A 6 μm diameter carbon filament (running from bottom left to top right) compared to a human hair.

Depending upon the precursor to make the fiber, carbon fiber may be turbostratic or graphitic, or have a hybrid structure with both graphitic and turbostratic parts present. In turbostratic carbon fiber the sheets of carbon atoms are haphazardly folded, or crumpled, together. Carbon fibers derived from Polyacrylonitrile (PAN) are turbostratic, whereas carbon fibers derived from mesophase pitch are graphitic after heat treatment at temperatures exceeding 2200 °C.

Turbostratic carbon fibers tend to have high tensile strength, whereas heat-treated mesophase-pitch-derived carbon fibers have high Young's modulus (i.e. high stiffness or resistance to extension under load) and high thermal conductivity.

Applications

The global demand on carbon fiber composites was valued at roughly US\$10.8 billion in 2009, which declined 8–10% from the previous year. It has been expected to reach US\$13.2 billion by 2012 and to increase to US\$18.6 billion by 2015 with an annual growth rate of 7% or more. Strongest demands come from aircraft and aerospace, wind energy, as well as from the automotive industry⁶ with optimized resin systems⁷.



Tail of an RC helicopter, made of Carbon fiber reinforced polymer

Composite materials

Carbon fiber is most notably used to reinforce composite materials, particularly the class of materials known as carbon fiber or graphite reinforced polymers. Non-polymer materials can also be used as the matrix for carbon fibers. Due to the formation of metal carbides and corrosion considerations, carbon has seen limited success in metal matrix composite applications. Reinforced carbon-carbon (RCC) consists of carbon fiber-reinforced graphite, and is used structurally in high-temperature applications. The fiber also finds use in filtration of high-temperature gases, as an electrode with high surface area and impeccable corrosion resistance, and as an anti-static component. Molding a thin layer of carbon fibers significantly improves fire resistance of polymers or thermoset composites because a dense, compact layer of carbon fibers efficiently reflects heat⁸.

The increasing use of carbon fiber composites is displacing aluminum from aerospace applications in favor of other metals because of galvanic corrosion issues^{9,10}.

Textiles

Precursors for carbon fibers are polyacrylonitrile (PAN), rayon and pitch. Carbon fiber filament yarns are used in several processing techniques: the direct uses are for prepregging, filament winding, pultrusion, weaving, braiding, etc. Carbon fiber yarn is rated by the linear density (weight per unit length, i.e. $1\text{g}/1000\text{m} = 1\text{tex}$) or by number of filaments per yarn count, in thousands. For example, 200tex for 3,000 filaments of carbon fiber is three times as strong as 1,000 carbon filament yarn, but is also three times as heavy. This thread can then be used to weave a carbon fiber filament fabric or cloth. The appearance of this fabric generally depends on the linear density of the yarn and the weave chosen. Some commonly used types of weave are twill, satin and plain. Carbon filament yarns can be also knitted or braided.

Microelectrodes

Carbon fibers are used for fabrication of carbon-fiber microelectrodes. In this application typically a single carbon fiber with diameter of $5\text{--}7\mu\text{m}$ is sealed in a glass capillary¹¹. At the tip the capillary is either sealed with epoxy and polished to make carbon-fiber disk microelectrode or the fiber is cut to a length of $75\text{--}150\mu\text{m}$ to make carbon-fiber cylinder electrode. Carbon-fiber microelectrodes are used either in amperometry or fast-scan cyclic voltammetry for detection of biochemical signaling.

Catalysis

PAN-based nanofibers can efficiently catalyze the first step in the making of synthetic gasoline (not to be confused with syngas) and other energy-rich products out of carbon dioxide. The process uses a “co-catalyst” system in three steps:

1. EMIM-CO₂ complex formation;
2. Adsorption of EMIM-CO₂ complex on reduced carbon atoms
3. Carbon monoxide formation.¹²

The first step uses an ionic liquid, while graphitic carbon structures doped with other reactive atoms replaced silver to produce the final output. The carbon nanofiber catalyst exhibited negligible overpotential (0.17V) for carbon dioxide reduction and more than an order of magnitude higher current density compared with silver under similar experimental conditions. The reduction derived from the reduced carbons rather than to electronegative nitrogen dopants. The performance came from the nanofibrillar structure and high binding energy of key intermediates to the carbon nanofiber surfaces^{12,13}.

Synthesis

Each carbon filament is produced from a polymer such as polyacrylonitrile (PAN), rayon, or petroleum pitch, known as a precursor. For synthetic polymers such as PAN or rayon, the precursor is first spun into filament yarns, using chemical and mechanical processes to initially align the polymer atoms in a way to enhance the final physical properties of the completed carbon fiber. Precursor compositions and mechanical processes used during spinning filament yarns may vary among manufacturers. After drawing or spinning, the polymer filament yarns are then heated to drive off non-carbon atoms (carbonization), producing the final carbon fiber. The carbon fibers filament yarns may be further treated to improve handling qualities, then wound on to bobbins¹⁴.

A common method of manufacture involves heating the spun PAN filaments to approximately 300 °C in air, which breaks many of the hydrogen bonds and oxidizes the material. The oxidized PAN is then placed into a furnace having an inert atmosphere of a gas such as argon, and heated to approximately 2000 °C, which induces graphitization of the material, changing the molecular bond structure. When heated in the correct conditions, these chains bond side-to-side (ladder polymers), forming narrow graphene sheets which eventually merge to form a single, columnar filament. The result is usually 93–95% carbon. Lower-quality fiber can be manufactured using pitch or rayon as the precursor instead of PAN. The carbon can become further enhanced, as high modulus, or high strength carbon, by heat treatment processes. Carbon heated in the range of 1500–2000 °C (carbonization) exhibits the highest tensile strength (820,000psi, 5,650 MPa or N/mm²), while carbon fiber heated from 2500 to 3000 °C (graphitizing) exhibits a higher modulus of elasticity (77,000,000 psi or 531 GPa or 531 kN/mm²).

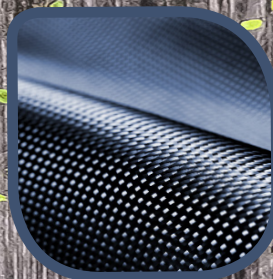
Manufacturers

Major manufacturers of carbon fibers include Toho Tenax, Cytec Industries, Formosa Plastics, Hexcel, Mitsubishi Rayon, SGL Carbon, Toray Industries and Zoltek. Manufacturers typically make different grades of fibers for different applications. Higher modulus carbon fibers are typically more expensive¹⁵.

Renewable fibre production research

Currently a number of research institutions are carrying out research to try to synthesise carbon fibre from renewable, non-fossil fuel based feedstocks^{16,17}. If successful this could reduce greenhouse gas emissions associated with carbon fibre manufacture as well as long term costs of production¹⁸.

The 12 Green Principles Applied to our Domains



1. Prevention



In inorganic chemistry the change of the 12 principles are demonstrated via **cement manufacturing**. The measurements regarding prevention are as follows:

- **Waste in the form of gases -> pass a filter -> only CO₂ is left**
- All gases released by the processes have to pass filters. This way, beside CO₂ all remaining gases can be transferred to non-hazardous gases (Denox-Process and adsorption of SO₂). Dust is removed by electrostatic precipitators.
- CO₂: 1/3 can be influenced but not be avoided by alternative fuels 2/3 from decarbonising (CaCO₃ -> CaO + CO₂)
- Ash from the filters can be introduced into the process.
- The process can use external waste, such as used tires as fuel
- Construction waste can be reused in the process

As for **organic chemistry** the manufacturing processes must be **designed to avoid waste and their subsequent recycling**. This principle can be described with examples of processes and procedures in the organic synthesis. In it harmful reagents are replaced by less toxic, more efficient and leaving fewer side products.

For example, **the phosgene**, used as the carbonating agent in some processes, is applied as a methylation agent, an alternative of the methyl chloride and dimethyl sulfate.

In oxidation processes, the use of stahimetricrhnite reagents such as potassium permanganate, potassium dichromate, the organic hyper oxides are less preferred than **the hydrogen peroxide**.

The replacement of chlorinated reagents with **non-chromium compounds** in chemical processes and bleaching technology in paper-producing and textile industry. This leads to a reduced formation of dioxins and chlorinated toxins.

The legislative control on the reduction of waste fundamentally changed the manufacture of **pharmaceutical** products. The recycling of a portion of the waste (e.g. regeneration of solvents) was in common practice due the economic reasons, but the spread of green chemistry resulted in the greening of further procedures.

The demand for technologies with lower waste production emerged, as the handle, storage and assumed conversion of the hazards severely decrease the financial efficiency of the procedures. Meanwhile no increase of control and checks can eliminate the possibility of leakage or accident.

The main aim was to lessen the environmental factor, since for some pharmaceutical products it can be over 100. Considering the output of chemical industries, pharmaceutical industry has the lowest one, while **the manufacture 1kg of effective substance also produce a 25-100kg of waste**.

To estimate the amount waste a regeneration practical of copper sulphate was carried out. A few grams of $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O} - \text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ mixture were converted to $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ producing 50-100cm³ of waste water, not considering recrystallisation.

According to Maurizio Chioetto, member of the Iso and Unichem, Astanalytyca commissions (Genova - Italy), nowadays **the presence of hazardous heavy metals - Pb, Ba, Ni, Ag, Co, Cu, Hg, Cr, and Mn - in marine waters** is one of the most worrying aspects of environmental contamination, in addition to the presence of organic substances and hydrocarbons, because of the toxicity of these compounds. During our lab activities at ITIS Pininfarina, we have developed a series of **experiments which avoided the use of heavy metals**. In Italy there are 2.500.000 students attending secondary education schools: if we suppose the use of 1 g of metal per student, we obtain the use of 2.5 tons metal per year that can be reduced!

Cosmetic industry formerly used a lot of formaldehyde, which is an organic compound with the formula CH_2O or HCHO . Both the International Agency for Research on Cancer (IARC) and the U.S. Environmental Protection Agency (EPA), have determined that excessive exposure to formaldehyde gas, especially over a long period of time, can cause cancer in a rare nasal form. While nail polish may contain chemical substances derived from formaldehyde, in its pure form, formaldehyde itself is not an ingredient.

Tosylamide/Formaldehyde Resin is a polymer formed from the reaction of toluenesulfonamide and formaldehyde. Tosylamide/Formaldehyde Resin is used in nail enamel products. It is a soft resin material which, in conjunction with nitrocellulose, forms tough, shiny and durable films on nails. Addition of Tosylamide/Formaldehyde Resin makes the film less brittle, tougher, and the resin also increases the gloss of the film. Tosylamide is also a bioaccumulative toxin that has a high tendency to cause allergic reactions in humans. Most nail care products nowadays don't have formaldehyde resins in their composition as they've been deemed too dangerous.

Nail products containing up to 12% Tosylamide/Formaldehyde Resin were no sensitizing, no photosensitizing and essentially non irritating to human skin. Reports of nail polish dermatitis of allergic origin have been attributed to Tosylamide/Formaldehyde Resin and other liquid thermoplastic resins.

Some people may have sensitivity to one or more of the different chemical components that make up these nail cosmetics. Sensitivity to the offending agent may cause allergic contact dermatitis and/or irritant contact dermatitis. In a study by the North American Contact Dermatitis Group (NACDG), Tosylamide/ Formaldehyde Resin was found to be the seventh most common ingredient causing allergic contact dermatitis in patients with a cosmetic allergy.

Nail compounds that are used to color the plate are generally referred to as nail polish, varnish or lacquer. Now Toluenesulfonamide/Formaldehyde Resin found in nail polish was changed with **acrylic resins**. Unfortunately, the polyester resin nail polishes do not perform as well as those containing Toluenesulfonamide/Formaldehyde Resin.

During the production of **carbon fibers**, there is no waste except **combustion gases**. These gases also, as mentioned above, are rendered harmless by burning.

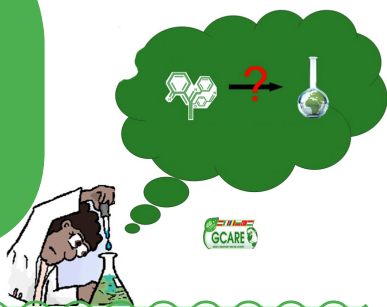
Due to heat treatment in the production process of carbon fibers, molecular structure elements other than carbon, combustible gases occur. These harmful gases can not be directly released to the atmosphere. **They must be burned in special combustion chamber and must be removed in a manner of appropriate to the definition of "Green Chemistry". Thermal Oxidizers are used for this purpose.**

Basic raw material of Carbon fiber is methyl cyanide (acrylonitrile). The polymer obtained by polymerization of acrylonitrile is converted to special fiber (precursor). Precursor fiber is converted to carbon fiber in two stages. At oxidation stage, the fibers are heated in air to 200-300 degrees centigrade. This process provides separation of H of fiber and addition of more volatile O to the fiber. The polymer turns into a stable ring structure from chain structure. During this process, the color of fibers from white to brown, then turns black.

3-5% mass loss occurs. The resulting gases are burned in incinerators (Thermal oxidizer) and is removed by environmentally benign structure.

At carbonization step in which Oxidized fibers is heated to 1200-1500 °C in an inert gas atmosphere and providing 95% of the fibers are carbonized. The honeycomb structure is formed of a molecular. 40 to 50% mass is lost in the process of carbonization. . The resulting gases is burned in incinerators (Thermal oxidizer) and is removed by environmentally benign structure.

2. Atom Economy



Design synthetic methods to maximize the incorporation of all materials used in the process into the final product.

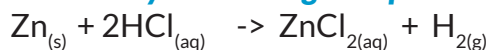
The production of a given effective agent is typically **a multi-step process**. Moreover the typical medication substances are organic compounds resulting in the issue of inevitable by-products at large-scale industrial methods. In case the product mixture needs to be separated, a new form expenses is created. **Ideal** green chemistry processes make all reactant atoms end up in the product molecule, which is hardly reached in multi-step reactions.

Therefore pharmaceutical reactions obviously display lower atom efficiency.

In order to study the efficiency CuSO₄·5 H₂O regeneration practice was carried. The used methods were compared and evaluated to each other paying attention to environmental factor (E), atom efficiency and production yield (%). A new recipe was set up, which was mainly used for the study of the first two principles, as larger scale practice was beyond our possibilities.

A **atom economy** asks the question: "what atoms of the reactants are incorporated into the final desired product(s) and what atoms are wasted?"

Traditionally, the efficiency of a reaction has been measured by calculating the percent yield. Let us assume that the following reaction, normally used in the laboratory to produce hydrogen, gives 100% yield. While this is admirable, we can shed more light on the **efficiency of a reaction by calculating the "percent atom economy"** as follows:



The nearer the value is to 100, the less the waste will be.

$$= (2,016/65,37 + 2 \cdot 36,461) \times 100 = 1,46\%$$

The percent atom economy is simply the formula weight of the desired product(s) divided by the sum of the formula weights of all the reactants, which gives 1,46.

In cosmetics an aerosol formulation consists of two components, the product concentrate and the propellant. The product concentrate is the active drug combined with additional ingredients or co-solvents required to make a stable and efficacious product. The concentrate can be a solution, suspension, emulsion, semisolid, or powder.

The propellant provides the force that expels the product concentrate from the container and additionally is responsible for the delivery of the formulation in the proper form (i.e., spray, foam, semisolid). When the propellant is a liquefied gas or a mixture of liquefied gases, it can also serve as the solvent or vehicle for the product concentrate.

A propellant is a chemical with a vapor pressure greater than atmospheric pressure at 40°C (105°F). When a liquefied gas propellant or propellant mixture is sealed in an aerosol container with the product concentrate, an equilibrium is established between the propellant which remains liquefied and a portion that vaporizes and occupies the upper portion of the container. Types of propellants commonly used in pharmaceutical aerosols:

In cement manufacturing, reaction proceeds with nearly 100% yield (beside the loss of CO₂!)

In organic chemistry, reducing the number of stages is an effective way to enhance nuclear economy. For example the traditional synthesis of the drug **ibuprofen includes six stages** with a total atomic efficiency, not exceeding 40%. In recent years, it has been developed **a three-step synthesis** of this analgesic and the atomic efficiency has reached 80%.

When pharmaceutical industry is discussed, it is often stated that each and every pill can be traced back to crude oil, since it is the major raw material of organic syntheses.

Type	Properties: Advantages & Disadvantages
Chlorofluorocarbons (CFC) such as P-11 (CCl_3F), P-12 (CCl_2F_2), and P-114 ($\text{CClF}_2\text{ClF}_2$)	<ul style="list-style-type: none"> • gases at room temperature • can be liquefied by cooling them below their boiling point or by compressing them at room temperature • their use severely curtailed due to their role in depleting the ozone layer of the atmosphere
hydrochlorofluorocarbons (HCFC) and (HFC) hydrofluorocarbons	<ul style="list-style-type: none"> • may not contain chlorine and have one or more hydrogen atoms • break down in the atmosphere at a faster rate than the CFCs resulting in a lower ozone depleting effect
Hydrocarbons e.g. Propane, butane, and isobutane	<ul style="list-style-type: none"> • used in topical pharmaceutical aerosols • because of their environmental acceptance low toxicity and no reactivity • the hydrocarbons remain on top of the aqueous layer and provide the force to push the contents out of the container
Compressed Gases: e.g. nitrogen, carbon dioxide	<ul style="list-style-type: none"> • small quantity relative to the composition of the product • suitability both for solvent-based and water-based products • non-flammable and safe during work, storage and use, with no danger of fire or ignition

Solution aerosols are two phase systems consisting of the product concentrate in a propellant, a mixture of propellants or a mixture of propellant and solvent. Solvents may also be added to the formulation to retard the evaporation of the propellant. Aerosol solutions have been used to make foot preparations, local anesthetics, sprays on protective films and anti-inflammatory preparations. It is used more in cosmetics products (deodorants, antiperspirants, hairsprays, hair foams, shaving foams etc). The particle sizes of the sprays can vary from 5 to 10 mm in inhalation aerosols and 50 to 100 mm for topical sprays.

In order to study the efficiency, ***CuSO₄·5 H₂O regeneration*** practice was carried. The used methods were compared and evaluated to each other paying attention to environmental factor (E), atom efficiency and production yield (%). A new recipe was set up, which was mainly used for the study of the first two principles, as larger scale practice was beyond our possibilities. For the ***domain of carbon fibers Atom economy can only be possible with the process of side-products and waste.*** Ensuring optimization of atoms provides efficient use of raw materials literally. Wasted each atom is useful for both the environment and producers. When producing the acrylic polymer are converted to carbon fibers, attention is given to efficient use of raw materials. Manufacturing processes without compromising basic characteristics of the carbon fibers are designed optimally. ***When the performance and the price comparisons are made, carbon fiber will replace the metals used in the composite materials quickly.*** Carbon fiber which is lightweight and durable product is used in many fields such as aerospace, defense purposes, clothing, automotive, construction, medical and paper industry.

The manufacture of carbon fibers, losing the other atoms heating the organic feedstocks other than carbon so that the resulting filaments are composed of carbon atoms are obtained. These filaments are obtained after crystallization of the high strength fiber.

The features of carbon fibers which are produced from Polyacrylonitrile fiber of vegetable-based raw materials, tar and the tar residue, the polyvinyl chloride or copolymers polivinildenklor vary depending on the raw material used, the temperature and production process. Properties of carbon fibers which differ according to production conditions and usage are different from each other

When producing the acrylic polymer are converted to carbon fibers, attention is given to efficient use of raw materials. ***Manufacturing processes without compromising basic characteristics of the carbon fibers are designed optimally.***

3. Less Hazardous Chemical Syntheses



Design synthetic methods to use and generate substances that minimize toxicity to human health and the environment.

n cement manufacturing dioxin formation is avoided by high temperatures -> prevented by chemical filtration. It is important to avoid chlorine as much as possible in the intake materials. Nevertheless a correct design of temperature levels and a fast temperature increase in the process have to follow to minimize the chance of forming VOCs (volatile organic compounds) and PCDD/PCDFs (Polychlorinated dibenzo-p-dioxin, Polychlorinated dibenzofuran).

A n example of this principle in organic chemistry is the technology of producing cumene. Cumene as a separate product is unnecessary, but is produced in very large quantities - about 7 mln. tons per year, because it is a source of the phenol and the acetone. The phenol is used as the disinfectant in veterinary medicine. Today, its use is limited and the triazol and bleach are used as its substitute. Phenol is a feedstock for the preparation of picric acid. One of its applications is its participation in the quality reaction for the determination of bile pigments in clinical trials on animals and humans.

Another example is the conversion of the ketone to lactone. This process takes place under the action of m-chloro-parabenzon acid. It is proposed a new method of carrying out the process with the use of baker's yeast as a biocatalyst and oxygen from the air as an oxidant. This example contains **2 "green" components - the catalyst and the air**, instead of an explosive and uneconomical oxidant. In the use of dimethyl carbonate in the methylation, instead of other methylation agents, produces an excess carbon dioxide which is more easily processed than the separation of the chlorine and sulfur-containing byproducts.

The hazards and pharmaceutical products first may appear controversial, but many production methods include hazardous chemicals. There are strict requirements for the product and the great amount of wastes produced suggests that the alterations of methods is required. Tendencies imply that newer generation of effective substances will help the industry turn greener. Meanwhile the demand of effectivity is accompanied by the dream of zero side-effects.

More and more pills are taken and mankind refuses older medicine due to the side-effects. **Sometimes total success is reached (analgesics from salicylates to ibuprofen)**, but many cases there is no possibility of fulfilling all demands: large-scale antibiotics could not overtake the lead from penicillin.

Ozone is used as a disinfectant for killing microorganisms in the air and water. Many spas and hot tubs use ozone to keep the water free of algae and harmful bacteria. Ozone is also used for industrial and manufacturing purposes, as well as a bleaching and deodorizing agent.

Ozone disinfection produces less disinfection byproducts which will enable these facilities to meet more stringent drinking water standards and regulations. Ozone also removes more trace organic compounds than chlorine which will result in better tasting and smelling water. **Today more than 500 municipalities around the world purify their water supplies with ozone**, including Los Angeles, Paris, Montreal, Moscow, Kiev, Singapore, Brussels, Florence, Turin, Marseilles, Manchester and Amsterdam.

Parabens are chemicals widely used as preservatives by cosmetic and pharmaceutical industries or as food additives. Their demonstrated utility as preservatives, low cost, long history of use and the inefficiency of some natural alternatives in many types of formulas, which made it very attractive for human use.

Parabens are organic-esters of para-hydroxybenzoic acid, from which the name is derived. All commercially used Parabens are synthetically available, although some are identical to those found in nature. They are produced, at industrial scale, by the esterification of p-hydroxybenzoic acid with an appropriate alcohol, such as methanol, ethanol or n-propanol.

Is the opinion of SCCS/1348/10 (Scientific Committee on Consumer Safety) that authorized maximum concentrations for Ethylparaben and Methylparaben: 0.4% for one ester or 0.8% when used in 17 combinations, is considered safe for human health. Studies indicate that Methylparaben applied on the skin may react with UVB leading to increased **skin aging** and **DNA damage** when exposed to sunlight. Parabens can also cause the **breast cancer**.

According to Legislation, Parabens can be used in maximum allowed concentration, but scientifically, until now, it wasn't demonstrated that Parabens are totally non-toxic for human health. **We can totally replace the Parabens or, better, we can totally replace the preservatives in cosmetic products.**

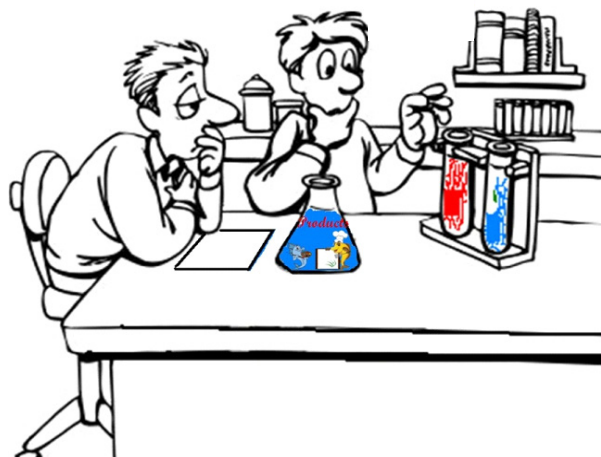
FARMEC Company already formulates a range of products Gerovital Plant - without Parabens, without preservatives - substances that can have potential adverse effect on human health.

Because acrylonitrile, which is the basic raw material of carbon fiber and flammable substance that has a negative impact on human health, the design of the production process of the acrylic polymer is immensely important environmentally. Therefore, the production of polymer is contemplated in accordance with this principle.

Carbon fibers are used in aircraft brakes and rockets in the formation of high temperature because they can not melt easily. The placement of the micro-structure of vertically and horizontally crystallites affects the features of the carbon fibers. The orientation of the microstructures can be replaced by plastic deformation or heat treatment.

4. Designing Safer Chemicals

Design chemical products to affect their desired function while minimizing their toxicity.



In the field of organic chemistry this principle is especially important in the creation of **pesticides** and other plant protection agents. If the mechanism of the **detergents** for protection is unclear, it is possible the target synthesis of the products only containing a functional group or a fragment of the structure, which is needed for the effective operation of the detergent. This way the toxicity of the detergent will be reduced.

In recent years methods have been developed for the preparation of **biodegradable polymers for packaging of the foodstuffs**. For example, the company “Dow Chemical” has developed the Nature Works polymer based on lactic acid. Another example is the replacement of the polyacrylic acid with polyglutamic acid by using the chitosan and cellulose derivatives.

The safety of pharmaceutical products is double-faced: efficiency and side-effects compete against each other. The goal of zero side-effects is present in pharmaceutical research. More and more pills are taken and mankind refuses older medicine due to its side-effects. It is outlined by the timeline of analgesics. Till the 19th century pain relief was based on opioids. The first written reference of opium dates from 5000 BC. In 1804 the active ingredient in opium was isolated and named morphium. This milestone indicates the beginning of the chemical industry.

Morphine's a high potential for addiction paved the way for salicylates. From the beginning of the 20th century aspirin got widely used, then paracetamol took over the market. By 1948 its had its side effects revealed. Today paracetamol continues to be used widely but scientist were worried about its effect on the liver. Large doses have been shown to cause liver failure. **The modern pain-killers contain ibuprofen, a carboxylate type of compound, just like aspirin.** Sometimes total success is reached, but many cases there is no possibility of fulfilling all demands: large-scale antibiotics could not overtake the lead from penicillin. Sometimes older effective substances are found to be efficient for new areas (Aspirin Protect).

An antifoulant is a substance that is coated onto ships' hulls and other water devices such as buoys to prevent microbial and plant growth (algae, barnacles, oysters, etc.). Besides potentially undermining the infrastructure, growth on hulls create drag, requiring the use of more energy and fuel to operate the ship. Ships have to be periodically scraped or dry docked and cleaned to combat this occurrence.

Antifoulants do not stay fixed on the hull forever; they enter the water and the aquatic environment. Once absorbed by organisms, they can potentially affect the ecosystem. Toxic chemicals can disrupt organism physiology and affect wildlife and human food supply. In 1970s, the principal antifouling substance employed was **tributyl tin (TBT)**, TBT is an example of an organotin, a substance that causes defects in marine organisms by disrupting endocrine and hormonal functions. The restriction and eventual **banning of TBT** created a demand in the market for more environmentally friendly products. However, almost a decade before TBT was banned; the company Rohm and Hass (now Dow Chemicals) had been searching for an environmentally friendly alternative. They screened and tested over 140 compounds, finally utilizing **4, 5-dichloro-2-octyl-4-isothiazoline-3-one (DCOIT) in a xylene solvent.**

FARMEC Company changes the formulation of their deodorants by replacing ethanol (VOC) with water (a non-toxic ingredient). A VOC is any organic compound having an initial boiling point less than or equal to 250°C (482°F) measured at a standard atmospheric pressure of 101.3 kPa and can do damage to visual or audible senses. [European Union] **Volatile organic compounds (VOCs) are emitted as gases from certain solids or liquids.** VOCs include a variety of chemicals, some of which may have short- and long-term adverse health effects. Concentrations of many VOCs are consistently higher indoors (up to ten times higher) than outdoors.

EPA's Office of Research and Development's "*Total Exposure Assessment Methodology (TEAM) Study*" (Volumes I through IV, completed in 1985) found levels of about a dozen common organic pollutants to be 2 to 5 times higher inside homes than outside, regardless of whether the homes were located in rural or highly industrial areas. TEAM studies indicated that while people are using products containing organic chemicals, they can expose themselves and others to very high pollutant levels and elevated concentrations can persist in the air long after the activity is completed.

The Volatile Organics Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution Concerning the Control of Emissions of Volatile Organic Compounds or Their Transboundary Fluxes (known as the Volatile Organic Compounds Protocol or the **VOC Protocol**) is a protocol to the Convention on Long-Range Transboundary Air Pollution which aims to provide for the control and reduction of emissions of volatile organic compounds in order to reduce their transboundary fluxes so as to protect human health and the environment from adverse effects. The protocol was concluded at Geneva, Switzerland.

- Opened for signature - November 18, 1991
- Entered into force - September 29, 1997

Acrylonitrile is mandatory to use in the production of **carbon fibers**. It cannot escape from it, **ATEX** (Atmosphere Explosive: Flammable and Explosive Atmospheres Security) and **HAZOP** (Hazard and Operability Study) studies which eliminate the negative effects and are assisted with the most advanced production design are being carried out.

5. Safer Solvents & Auxiliaries

*Minimize the use of auxiliary substances wherever possible
make them innocuous
when used*



There are no auxiliary substances used in **cement manufacturing**, and thus there is no bad influence on the environment.

In recent years the market offers new solvents which have an advantage over traditional ones. The processes of **organic synthesis** in water are environmental friendly and the purest and they are gradually taking good positions. As an example we can include the condensation in the presence of the **indio-containing catalyst** in the aquatic environment. We will notify the catalyst recycling in this process. There are organic syntheses without the presence of a solvent. This can be carried out on the conditions of **microwave activation**, which selectively heated polar fragments of the molecules and helps to accelerate and perform the processes. Thus, the secondary spirits with high selectivity can be converted into ketones in the presence of an iron catalyst - clay.

Pharmaceutical industry has a lot to do about the fifth principle. Studies showed that their liquid waste of pharmaceutical companies is 85% non aqueous. Some solvents were banned so they have to be replaced in organic syntheses because of their **high toxicity**. These include the formerly widely used **Chloroform** and **carbon tetrachloride**. Other typical solvents are still in use in spite of their known toxicity: **cyclohexane** and **toluene**. The reduction in the use of organic solvents is an important issue and a lot of research is done. **The green solvents include water, acetone, ethanol and ethyl acetate . New organic synthetic routes with minimum of "zero" solvents are in the research stage.** Ibuprofen is an up-to-date pain-killer is one the greatest successes of Green Chemistry. It was first synthesized in 1960 in six steps. Nowadays the modern method uses 3-steps with one step of aqueous media.

Clorinated solvents represent one of the principal forms of **pollution of underground waters** because of their great diffusion as they are largely employed as degreasers for electronic and mechanical parts, to clean metals and clothes (laundry), or as solvents and raw materials in the chemical-pharmaceutical industry (drugs, paints, coatings and glues). In our city area (Torino), the water contamination is important, as a matter of fact, out of 35 monitored areas, the presence of chlorinated solvents has been detected in 19 areas with a more or less continuous percentage. **It is absolutely necessary to employ alternatives such as supercritical fluids and ionic liquids.**

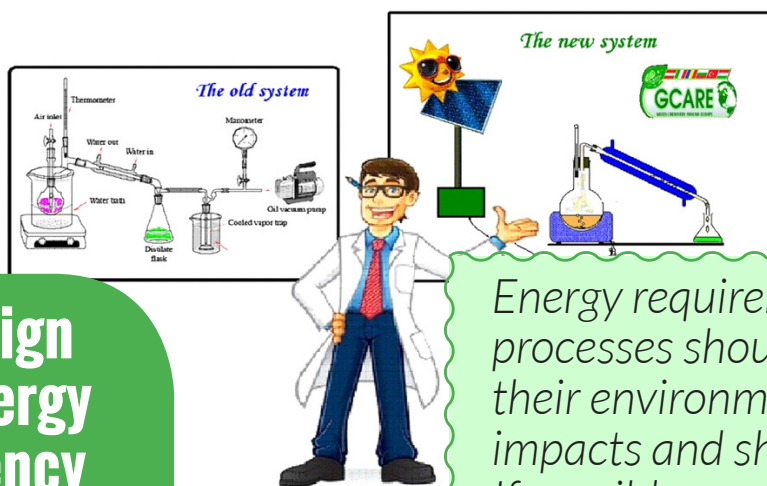
Oxybenzone or (2-hydroxy-4-methoxy) benzophenone is an organic compound used in **sunscreen products** of cosmetic industry. It is also used as an ingredient in sunscreen products and other cosmetics because it absorbs in UVB and short-wave UVA (ultraviolet) rays. Oxybenzone was one of the first compounds incorporated into sunscreen formulations to offer enhanced UVA protection because its absorption spectrum extends to less than 350 nm. Oxybenzone's ability to absorb UV rays is due to a variety of molecular interactions.

According to The Skin Cancer Foundation, old research on rodents suggested that oxybenzone, a synthetic estrogen, can penetrate the skin, may cause allergic reactions, and may disrupt the body's hormones, producing harmful free radicals that may contribute to melanoma. However, there has never been any evidence that oxybenzone, which has been available for 20 years, has any adverse health effect in humans. In the products from EU market, intended for skin protection with 0.5% or more oxybenzone, must be labeled as "contains oxybenzone". **FARMEC Company has already designed new formulation for sunscreen products that contain no oxybenzone.** The sunscreen products have other UV filters that provide protection against harmful effects of UVA/UVB radiations.

As producing carbon fiber, material selected as the polymer solvent is an amide, **hazard level is low.**

Carbon fiber, an inorganic material is not affected by humidity, outdoor, solvents, bases and weak acids at room temperature. But rather than being affected by oxidation at high temperatures. Silizium that, Boral, the siczn, sibcn, sico, silicone or phenolic resins by binding the SiC composite by coating the liquid phase process carbon fiber and the metal matrix reinforced with fibers can be obtained at low cost. Metal matrix composites reinforced with fibers, the fibers are well protected against high static strength metal matrix fiber while external influences. Such composites have good mechanical properties at high temperatures, high hardness, high strength shows a good degree of stiffness and resistance to oxidation and corrosion. Conventional granular activated carbon fibers of higher specific surface area than carbon fibers and has a higher absorption and desorption rates. Phenolic specific surface area of activated carbon manufactured from the resin is higher. 300 C was performed using pre-oxidation process coal production amount of activated carbon fibers produced from the tar can be improved. Methane absorption capacity was examined when the pore size of the carbon fiber was found to be maximum when the 1-2nm.

6. Design for Energy Efficiency



Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

In cement manufacturing (inorganic chemistry) design for energy efficiency works as follows:

Temperatures of 1500°C are required to burn the clinker.

There is no way to reduce the energy consumption, but there are possibilities to use waste as fuel for the process, for example: used tyres, waste oils, sewage sludge, rubber, waste woods, plastics, paper waste, paper sludge, spent solvents.

As the whole process runs under normal pressure, there is no possibility, to improve the energy consumption by reducing the pressure.

In organic chemistry the use of catalysts, microwave irradiation (for heating), the use of parallel circuits in which the heat from the exothermic reaction is absorbed by the endothermic reaction.

For example, in the dehydrogenation of the ethyl benzene to styrene, and the hydrogenation of the nitrobenzene in the first process it releases hydrogen.

The implementation of the process at low pressure and temperature is an important step towards savings resources.

Energy saving in pharmaceutical industry is an important issue. Fuel supply and oil prices may pose extra expenses onto the companies. **Heating, Ventilation and Air Conditioning (HVAC) is typically the largest consumer of energy.** Strategies for energy efficiency are continuously constructed for companies working in the drug industry today. The Environmental Protection Agency (EPA) is also working with Argonne National Laboratory to develop an energy performance benchmarking tool for pharmaceutical plants (see “Will Pharma Wear the Energy Star?”). For more information, please visit www.energystar.gov.

The possible solution is the “systems approach”, an over-all look at the entire motor system. Energy efficient operation include sizing, belt drive replacement and maintenance, which can save from 2% to 30% of total motor system energy use. Replacing an old motor with a high-efficiency motor is often a better choice than rewinding a motor.

Compressed air is required for many pharmaceutical manufacturing applications, including equipment operation and vacuum cleaning. It often comes in contact with products, for instance in packaging. It is often filtered to meet strict contamination control standards. **Despite of its importance, low energy-efficiency of only around 10% characterise the applications.** Therefore sparing use and constant monitoring of use are required. There are some techniques available to spare up to 20-50% based on the application.

Cosmetic companies, as chemical process plants are complex and **present an opportunity to minimize energy usage and maximize energy recovery through advanced process control (APC)**. APC involves installing hardware and software for capturing process operating data, analyzing trends and developing strategies to optimize control of all relevant variables.

Motors systems are widely used in the chemicals sector to drive pumps, fans and air compressors. Because of their extensive use, they provide excellent opportunities for energy savings. It is also possible to cost effectively improve the energy efficiency of boilers. **Optimizing these technical systems, when coupled with best practice motor management, can generally deliver energy savings of between 30 to 60% cost effectively.**

A large proportion of energy used by chemical companies is related to the operation of furnaces and boilers. The efficient use of this equipment depends on good control and regular maintenance to reduce energy wastage in steam distribution.

Recover waste heat and ensure boilers have condensate return. Energy and water loss can be minimized by using steam traps, which collect condensed water and return it to the boiler. This saves water and helps to conserve the heat of the water in the boiler, because the returned condensate is much hotter than feed water and may not require treatment.

Energy efficiency is an important competitiveness factor for the European chemical industry. The sector has constantly decreased its energy intensity over the past years. For reducing the energy consumption **FARMEC Company introduces cold processes for the production of cosmetics and house-hold products.**

Due to high temperature, both **oxidation and carbonization step** in the production of carbon fiber cause excessive energy consumption. Therefore the energy used (usually electric power) is important to be cheap and easily obtainable. The process is designed according to the principles of the energy recovery. The process is designed according to the principles of the energy recovery. Nevertheless, **it is inevitable to use high energy requirement and in the following manufacturing stage.**

CARBON FIBER PRODUCTION

Orlon, nylon, and some other kinds of physical and chemical applications as tar material with “carbon fiber” material created called. Elastomers based on use of the tar substances and substances are divided into two types of carbon fibers; Tar-based and PAN (Orion) based carbon fibers. Tar based carbon fiber production was 6% of world production, the production of carbon fiber-based Pan is up to 94%.

Pen production: Carbon fiber, the production-based Pan takes place in four main stages: oxidation and carbonization, the surface treatment and coating.

Oxidation: Orlon material in the oxidation step is heated to 300 ° C. Hydrogen material in the material decomposed in the heating step is added to the oxygen material. Thus, the carbon fiber to be produced in fire-proofing is gained.

Carbonization: Elastomers in coil carbonization step are heated up to 3000 ° C. Meanwhile, 100% carbonized material is provided. Class of carbon fiber produced by the high temperature in this process is given.

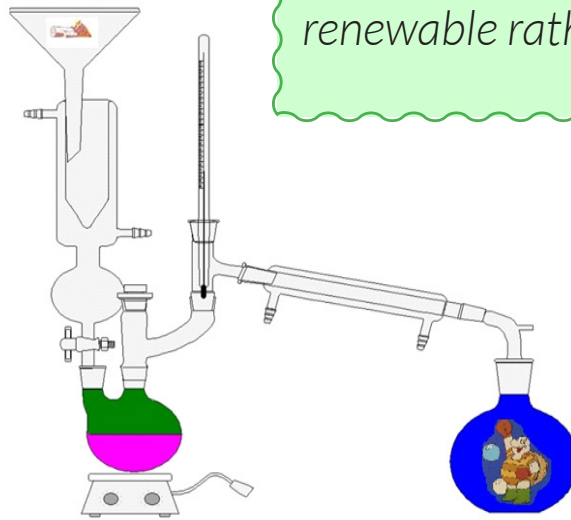
Surface Improvement: Orlon surface of the coil during the improvement in the electrolytic environment improved prescription for better adhesion.

Covering: Orlon processed during the coating step is coated with resin. Thus, PAN-based carbon fiber production is completed.



Whenever it's possible, technically and economically, a raw material should be renewable rather than depleting.

7. Use of Renewable Feedstocks



In cement manufacturing no renewable feedstocks are possible since 80% of the mining material consist of rock.

Additives can be varied:

Crushed brick of pulled down houses => reuse of building materials

In organic chemistry there is a trend of oil and natural gas depletion. Of the great importance is **the strategy for transition to renewable raw materials (plant, natural)**. The most suitable are vegetable oils - palm, cellulose, chitin and chitosan, its derivative, and the biomass.

An example of such approach is the bio catalytic process:

- preparation of pyrocatechol of D-glucose;
- preparation of ethanol by the reaction of the yeast.

Our pharmaceutical investigations involved the study of natural iron supply for principle 7. Iron deficiency is an ancient problem. The most typical symptoms are fatigue, and unusually pale skin, brittle nails and frequent infections. The sickness is called **anemia**. Anemic blood contains little amount of red blood cells. Red blood cells need iron. On average adults require 14,0mg of iron each and every day. The most iron rich food sources are peanut, poppy seed and mushroom. But you cannot eat a lot of peanut or poppy seeds day by day. Typical sources are dark chocolate, red meat and strawberry. Iron take-up requires additional vitamins, for example **vitamin C** or folic acid. In our practical broccoli and Béres csepp, a traditional Hungarian vitamin and mineral supply were studied.

At winter-time a good supply of ascorbic acid is necessary against cold and flu. **We decided to analyse the vitamin C content of typical winter-time natural sources: Californian or red sweet pepper, lemon and rose-hip.** First vitamin C is extracted from the sources and the content is measured by comparison to a standard vitamin C pill. The practical faced many difficulties due to the heat sensitivity of ascorbic acid. For some samples the results mirrored the official data at least in orders of magnitude.

Package and cosmetic products cannot be separated. FARMEC Company offers Nufar Green, a range of cleansing products with recyclable packaging. To properly recycle paper and cardboard packaging, we must ensure that we collect separately. At the collection centers, the paper, the boxes and the cartons are made packages, are pressed and then they are sent to paper mills to be recycled there. There, they are sorted into categories: newspapers, magazines, cartons etc., then chopped and mixed with water until a pulp is obtained.

Food cartons are placed in a container with water which is stirred for 15-30 minutes to separate the pulp from other materials. Pulp is washed and dried, the result being recycled paper. The paper obtained is used for the manufacture of other paper products: bags, newspapers, shops, envelopes, notebooks, egg cartons and even toilet paper.

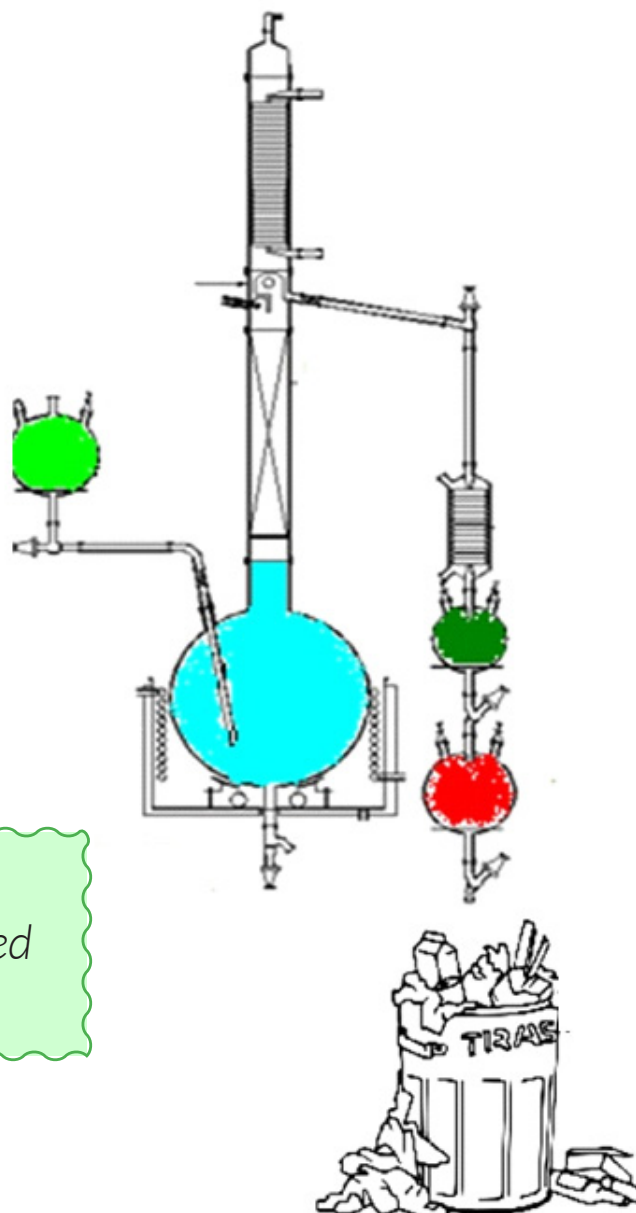


Considering both cosmetic and pharmaceutical industries the use of plastics offers a possible way of renewable feed-stock. Plastic recycling is the process of recovering scrap or waste plastic and reprocessing the material into useful products, sometimes completely different in form, from their original state. For instance, this could mean melting down soft drink bottles and then casting them as plastic chairs and tables. Plastics are also recycled/reprocessed during the manufacturing process of plastic goods such as polyethylene films and bags.

Before recycling, most plastics are sorted according to their resin type. In the past, plastic reclaimers used the resin identification code (RIC), a method of classification of polymer types, which was developed by the Society of the Plastics Industry in 1988. For example, polyethylene terephthalate, commonly referred to as PET, has a resin code of 1. Most plastic reclaimers do not rely on RIC now. They use automatic sort systems to identify the resin, such as near infrared technology (NIR). Some plastic products are also separated according to color before they are recycled. Then, they are shredded. The shredded fragments are subject to a process of elimination of impurities (like paper labels). This material is melted and often extruded in pellets which are then used to manufacture other products.

8. Reduce Derivatives

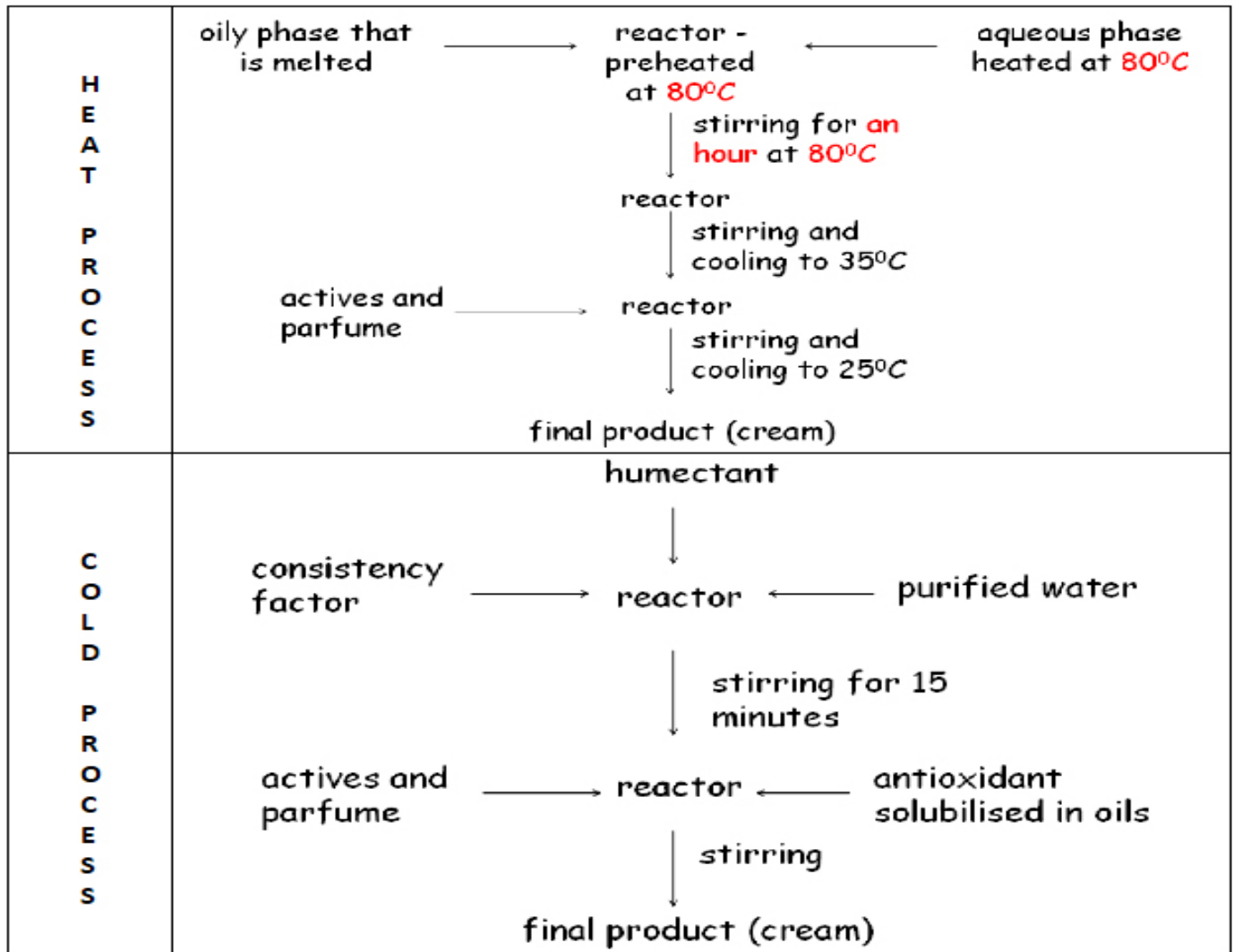
Unnecessary derivatization should be minimized or avoided if possible



Many processes of organic synthesis, particularly in the pharmaceutical, perfumery and grocery industry include a large number of protective and blocking groups which did not remain in the composition of the final product. Scientists have been developing highly selective processes and catalysts that eliminate inefficient stages.

In recent years achievements in enzyme catalysis have been implemented.

F ARMEC Company has created formulations that have cold production processes. The Average contains creams that have cold processes unlike other types of creams.



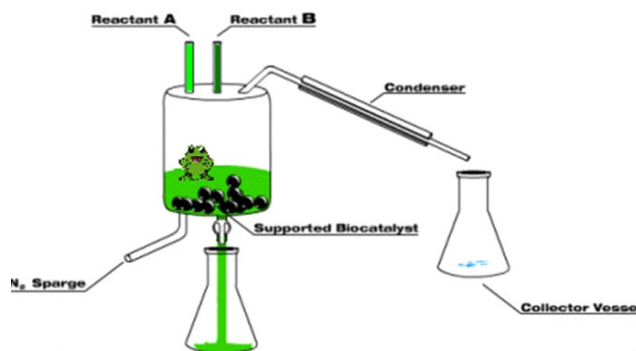
Conclusions

time economy - for producing a cream, a cold technological process it lasts approximately about 2 hours and a heat technological process it lasts approximately about 3 hours.

electric energy economy - for a cold technological process it is needed less energy than for a heat technological process.

9. Catalysis

Catalytic reagents are superior to stoichiometric reagents.



In cement manufacturing, catalysis is not yet in use and even **not applicable** in the production process. In case of exhaust systems the example is as follows:

- **Exhaust systems:** Reduction of NO_x in the exhaust system with the DENOX
- **Process:** In the SNCR process instead of urea ammonium sulphate can be used.
- SNCR (Selective non-catalytic reduction) can be replaced by SCR (Selective catalytic reduction)

In organic chemistry the combination of different approaches, such as the combination of the biocatalysis and electrochemistry with the conduct of proceedings in the aquatic environment; phase transfer catalysis and others. It is used the concept hypercritical (supercritical) fluids - these are liquids or gases used in certain temperature and pressure, conducted on unusual condition.

Catalytic processes in supercritical substrates. As substrates can be used hydrocarbons (olefins, paraffins, aromatics), for which the critical conditions are reached at relatively low pressure and temperature (to 40-80atm and to 200-300°C). In the past century supercritical fluids began to be used in the production for extraction of caffeine from coffee and tea.

In supercritical fluid it is reached the best combination of useful properties of gases and liquids - a high diffuse capacity, high density, ability to dissolve non-polar substances including the hard ones.

The ionization potential of substances in supercritical fluids is substantially lowering, so we can expect increasing the ability to react of many organic substances.

We know a lot of examples of catalytic reactions in supercritical environments - the hydration of olefins, polymerization and polycondensation and others.

The long range of different pharmaceutical products cannot be produced without catalytic reactions. Catalyst is a substance which speeds up the reaction. It's a key to the alternative pathway by decreasing the activation energy. There are many different reactions and many different catalysts. A specific catalyst works for particular reactions. **Catalysis is the most researched area of pharmaceutical chemistry.** Catalysts are very expensive, so reuse is very important. The aim is to regenerate every molecule of the catalyst.

Enzymes took their share of catalysis, because they are the most specific catalyst. **In pharmaceutical catalysis enzymes are happily used, because they are natural substances.** The substances bond to the active centre of the enzyme molecule. Enzymes have very specific three dimensional structure for their active centres, that's why only a particular compound can bond to it. The precise 3D structure plays an important role in pharmaceuticals.

For aspirin synthesis we tested some of the low-cost catalysts which were available: phosphoric acid, sulphuric acid and calcium carbonate and microwave techniques. The acidic catalyst performed well, but calcium carbonate proved to be a very good catalyst because:

- it is cheap
- available in our labs in huge amounts
- some dorps acid remove it
- the necessary amount is 0,02-0,04mg

There were two methods. The traditional method used water as auxiliary substance and 1.67 millimol of salicylic acid. The microwave method does not use auxiliary substances. We checked 3 different scales. The amount of acid catalyst is 1 drop. Microwave is not a typical catalyst, but changes the reaction to a great extent. Some say it is dangerous, but there is no clear scientific evidence. Microwave produced no results with the smallest scale, and greater amounts produced polymers. How microwaves work? Microwaves increase the molecular vibrations. It was very easy, but the acetic vapour is smelly. The catalyst free method is working in microwave. Microwaves spared energy, time and acetic acid anhydride in our practical.

Currently, different molecules flow into the water supply from medications, waste, purifiers, and other hosts. Many of these molecules have detrimental effects on not only humans that drink the water, but also on the aquatic life that lives in the water.

Terry Collins (Carnegie Mellon University) has focused his research on endocrine disruptors, which are some of the most harmful toxins currently being excreted into the water supply. He has developed environmentally safe oxidation catalysts (tetra-amido macrocyclic ligand **TAML®**) that can be used to decontaminate biological weapons, such as anthrax, and eliminate toxic residues produced by several industries.

Because chlorine is used predominantly for oxidation, he thought it might be possible to approach the problem overall by seeking out alternative oxidants. One of the great oxidants available is hydrogen peroxide. However, it is not an efficient enough oxidizer for most industrial applications. The new catalyst increases the efficiency of hydrogen peroxide. The TAML catalysts that Collins has developed are now rapidly being commercialized for the **replacement of chlorine** in a number of oxidation applications, such as pulp and paper, fabric treatment, and disinfection.

Advantages of the use of catalysts in industrial reactions are:

- It reduces the energy consumption that is necessary for a chemical reaction.
- Even if the catalyst does not participate directly in the reaction, after a number of uses, it is exhausted and must be replaced. A catalyst can be used many times. If the using time is greater than 10⁶, the catalyst is considered to be a catalyst with long life.

Catalytic oxidation is more advantageous than the stoichiometric oxidation. The stoichiometric oxidation reaction is less efficient than the catalytic reaction.

For this example, we can see the synthesis of methyl-phenyl-ketone.

Traditional method	Catalytic method (green)
$3C_6H_5CH(OH)CH_3 + 2CrO_3 + H_2SO_4 \rightarrow 3C_6H_5COCH_3 + Cr_2(SO_4)_3 + 6H_2O$	$3C_6H_5CH(OH)CH_3 + \frac{1}{2} O_2 \rightarrow C_6H_5COCH_3 + 6H_2O$
<p>The following disadvantages arise stoichiometric:</p> <ul style="list-style-type: none"> • high consumption of the reagent • hazardous working conditions • oxidants with toxic properties • toxic residues • less than half the amount of atoms in the reaction are in the final product 	<p>Catalytic method has the following advantages:</p> <ul style="list-style-type: none"> • just as an oxidizer, it consumes the oxygen in the air • is working in hazardous conditions • residues are friendly with the environment • the proportion of atoms in desirable finished product is really great.

For getting many useful pharmaceutical products, detergents or classes of food additives, is the process of oxidation of organic compounds. In this process are used strong oxidants such as per acetic acid, that can produce dangerous phytosanitary residues.

Green Variant should use oxygen in air. This has become possible thanks to nano-catalysts, soon made up of gold nanoparticles moles, 25 nm in diameter, which can activate the oxygen in air at low temperature of 60-80°C and pressure.

Biodegradable sheet was prepared in the laboratory from natural raw materials: gelatin, glycerin, natural dye in beetroot, distilled water.

We monitored the level of degradation of biodegradable film for over 150 days. Degradation of biodegradable film was noticed after 60, 90, 120 days, after 150 days the degradation was total.

The experiment demonstrates the opportunity of using biodegradable made materials from renewable raw materials, such as polymers to reduce environment pollution.

These materials either dispersed or degraded in the environment under the action of external agents: light radiation, absorption of water, oxygen, enzymatic attack or decompose by microbial degradation into their basic elements: CO₂, H₂O and biomass in a global cycle without create environmental problems and without requiring high costs.

Worksheet Obtaining Biodegradable Film:

*The purpose of the work:
obtaining film of biodegradable gelatin and glycerin*

Needed tools:

- palette
- berzelius beakers
- graduated cylinder
- funnel
- glass
- shaker wand
- pipettes
- scales
- glasses

Needed raw materials:

- gelatin
- glycerin
- natural dye from beetroot
- distilled water

Way of working:

- in a beaker introduce 4 grams of gelatin and 50 ml glycerin solution 1%
- shake the mixture obtained
- heat the mixture obtained to 95°C
- shake again to complete the solubilizing of gelatine
- slowly pour the solution obtained on a tray
- color with the natural dye from beetroot
- dry at room temperature
- follows the biodegradability of the film compared to the non-degradable films



Preparation of the mixture



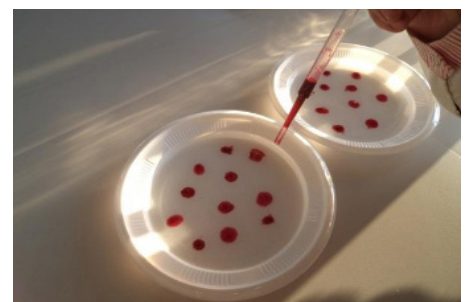
Solubilizing the glycerin



Tinting



Drying the biodegradable film



Decomposition of biodegradable film



10. Design for Degradation

Design chemical products so they break down into innocuous products that do not persist in the environment.



Degradation may refer to:

Biodegradation = the processes by which organic substances are broken down by living organisms

Chemical decomposition = the degradation of chemical compounds

Environmental degradation = the damage to the ecosystem and loss of biodiversity

is the process by which a chemical compound is reduced to a less complex form.

the degeneration of a chemical substance, of its physical properties or of its appearance (such as a plastic) is due to exposure to light, heat, oxygen or other reagents.

In cement manufacturing it is part of the technical demand of cement, that it shall not be degradable. Recycling of construction waste already takes place. The main part is used as a replacement of crushed rock in road works.

In organic chemistry this principle deals particularly with **the production of biodegradable products.**

A biodegradable product has the ability to break down, safely and relatively quickly, by biological means, into the raw materials of nature and disappear into the environment. These products can be solids biodegrading into the soil or liquids biodegrading into **water**. To be truly biodegradable, a substance or material should break down into carbon dioxide (a nutrient for plants), water and naturally occurring minerals that are not harmful to the ecosystem.

There are two types of alkyl benzene sulfonates, ABS (branched alkyl benzene sulfonate) and LAS (linear alkyl benzene sulfonate). LAS had not been discovered when ABS was first introduced as a detergent surfactant in the late 1940s. While ABS has served consumers well, foam-related environmental problems began to appear in surface waters, groundwater, drinking water and in wastewater treatment plants. Investigation of these problems led to the discovery that **ABS is resistant to biodegradation**. This resistance caused ABS to be known as non-biodegradable or a “hard detergent.” **LAS is known as biodegradable or a “soft detergent”** because it quickly and easily biodegrades and does not cause such environmental problems.

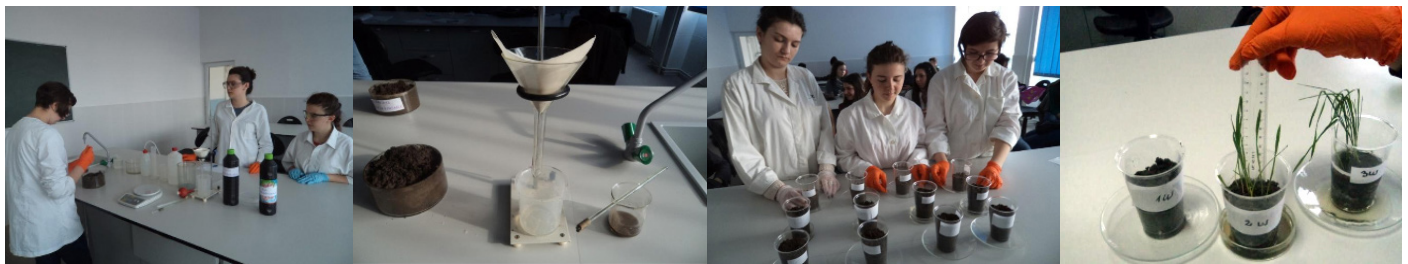
The GCARE project team with domain of cosmetics has conducted **several experiments to test product biodegradability for the comparison of Nufar Descalers**. A traditional cleaning product and biodegradable (without hydrochloric acid and without sulphuric acid) were investigated. **It observes a latency period of 7 days followed by a period of 21 days of degradation, maximum rate of degradation is 88.4% after 30 days.**

What we did for demonstrating the biodegradability of FARMEC Company cleaning products? We examined effects on the soil and plants. We studied two types of cleaning product (detergents), biodegradable Nufar Descaler and non-biodegradable Nufar Descaler.

We prepared three sets of soil samples:

- soil 1 - treated with biodegradable cleaning product
- soil 2 - treated with non-biodegradable cleaning product
- soil 3 - untreated soil.

We examined the pH of soil. We weighed 10 mg soil, added 50 ml of 0.1N KCl solution and stirred for 15 minutes. We filtered and determined the pH with pH meter. We repeated the determination after 7 days, 10 days and 21 days. For the soil 1 the pH grew up, after 21 days it was almost neutral. For the soil 2, the pH was acid (pH = 4,88). For the soil 3 the pH was constantly neutral. To highlight the effect of detergents on plants, we planted seeds of wheat and tomatoes in 3 soil samples.



Carbon Fiber is a type of fiber over 1000 years of life. The degradation of fiber manufacture with the following methods may be presented as an indication of whether the short-term.

PRODUCTION METHODS

Hand lay-up method: Mold is required to prepare the composites. Once deleted, the inner surface of the mold is cleaned with wax as the first separator. Then, the second separator is applied PVA. Afterwards the high viscosity of the resin applied by brush is prepared by cutting the fibers. Gel coat resin is spread and placed on the reinforcing element in the form of a felt or fabric. Thoroughly impregnated with resin brush strokes, it is provided to keep air bubbles using a roller. This process is continued until the desired thickness is provided. Most polyester and epoxy resins are used in this method. It is removed from the mold after hardening expected. This method is labor intensive and a method suitable for a small number of parts.

Spray Method: Hand lay-up method of instrumental acceptable form. Hand lay-up molding method similar to open lower on moderate volume and boats and boats, tanks, shower unit and shaped better than the larger complex hand lay-up techniques this technique. The advantage of this technique is simple; cost is low, the absence of the portable device and part size limitations.

Ready Molding Method: It is faster than other methods. A lot of products ranging from children's toys to aircraft parts can be produced with this method.

Resin Transfer Molding Method: This method, complex parts can be produced. Some parts are prepared in this way in the Formula 1 car.

Profile Drawing Method: As a resin material in this method is generally polyester, vinyl ester and epoxy is used. Continuous fiber material is used as a reinforcement material.

Filament Winding Method: Products made by this method: the missile pipes, pipes for oil transport, or poles, air, water tanks, sporting goods and so on.

Layered Combination Method: Between two heated mold surfaces shaped staple with open structures is produced in accordance with the hot-pressing method. Front embedded fibers (prepreg) saturated with resin are extruded or wrapped produced.

11. Real-time Analysis for Pollution Prevention

It is better to prevent waste than to treat or clean up waste after it has been created.



In cement manufacturing, the use of prompt gamma neutron activation analysis (**PGNAA**), which applies online measurement in the process, makes it possible to mix different qualities of raw products to avoid deviations in the production process and to avoid corrections at a late stage or reject of material.

In organic chemistry this principle is very important. In a factory of the company Union Carbide during the synthesis of **methyl isocyanate from phosgene many people died**. Later the company Du Pont has developed a new environmentally friendly method for the **preparation of methyl isocyanate without phosgene**. Of particular interest are the processes based on bio catalytic technologies, implemented on certain conditions and high selectivity.

Good news of finding cures for different diseases and illnesses often hit the screen in news programs. But **it takes such a long a time to make the pill available**. The reason is encoded into the medication molecules itself. The effective substances of pharmaceutical industry are all complicated structures with special 3D look. **Catalysis** is used to produce the special structure of the molecule directly. 3D structures gained public attention in the 60's when **Contergan**, a pill for pregnant ladies changed its precise structure and caused severe **mutations**. A Contergan-baby had problems with its limbs. The arms and the legs were shorter and parts were missing.

Surface water resources are often vulnerable to **contamination phenomena**, whether due to natural causes or to accidental spills.

The best approach in water quality control is the so-called **on-line monitoring technique**, which makes it possible to evaluate the conditions of the water on a continuous basis, in a fully automated manner and by means of highly advanced equipment.

This method gives real time data and ensures the possibility of taking immediate action to confine possible contamination sources and cope with emergency situations.

Acetone (systematically named propanone) is the organic compound with the formula $(\text{CH}_3)_2\text{CO}$. Because FARMEC Company respects and takes care of health and environment, it produces products that contain less hazardous substances and non-hazardous substances as many as possible. FARMEC Company is trying to produce products that after using will not remain as environmentally hazardous compounds.

FARMEC Company produced a cissolvent without acetone. By using this two-phase nail polish remover, with a modern formulation, the nails will become more resistant and more elastic => it brings benefits. The lack of acetone from its formula makes this solvent less aggressive and it ensures a healthy cleaning of the nail. The ingredients are ethyl acetate (solvent) and castor oil and wheat germ oil (hydrating agents).

When producing **carbon fibers** consisting of **waste gases are continuously monitored** and kept under control. Absolutely not allowed to move outside of the legal limit. Advanced measurement methods are used.

12. Inherently Safer Chemistry for Accident Prevention



Choose substances and the form of a substance used in a chemical process to minimize the potential for chemical accidents, including releases, explosions, and fires

In cement manufacturing, the only toxic substance for workers, processing cement is **chromium (VI)**. Reduction with iron or tin sulphate to chromium (III) takes place. The reducing agent is used in excess. **For workers safety, the expiration date has to be followed.**

Alkaline chemical burns. The chemical reaction to calcium hydroxide is not avoidable.



Workers have to wear proper safety clothes.

A n incident in the factory in Bhopal, India in 1984 killed 3,000 people on the day of the accident and 15,000 afterwards. At the time, the factory of the company Union Carbide was producing **Sevigny insecticide** (carbaryl, 1-naphthyl-N-methylcarbamate). This pesticide is produced after the reaction of the methyl isocyanate, \rightarrow - naphthol in an environment of 4-chlorine carbon. The unsafe production is considered as one of the reasons.

Fire or explosives are not used for the accident prevention. The organic compounds are not used in high concentrations. In chemical production there **is an obvious need of online monitoring processes**, of all inflows and outflows, including those, discharged into the atmosphere, soil and water. Scientists have developed **very sensitive and expressive methods of analysis for these purposes.**

P harmaceutical companies have always played an important role in society. That is why, environmental protection is of great importance. Nowadays, companies are focusing on prevention and are continually trying to cut the effects of their activities on the environment. These changes were supported by **the strict laws of environmental protection, the more expensive ways of waste treatment and the regular and rigorous control from the authorities all helped these changes.** More and more chemicals are being banned to protect not only the environment but also the employees and residents and to avoid industrial accidents.

Between 1932 and 1968, **a factory producing acetic acid discharged waste liquid into Minamata Bay, Japan. The discharge included high concentrations of methyl mercury**, increasing as the industrial activity expanded with production of polyvinyl chloride, using mercury as a catalyst. The Bay was rich in fish and shellfish, providing the main livelihood for local residents and fishermen from other areas. For many years, no one realized that the fish were contaminated with mercury, and that this was the cause of **the strange disease that appeared in the local community** and in other districts where the discharge reached the fish population. Minamata disease reached high levels in the 1950s, with severe cases suffering brain damage, paralysis, incoherent speech and delirium. Because the disease seemed to affect whole families and their neighbours, an infectious cause was suspected, especially when cats also became sick and died.

The disease was officially recognized in 1956 but epidemiological studies were slow to start and incomplete. Mercury poisoning was suspected in 1959 when sediments and shellfish from the Bay were found to have high levels, but this was not officially recognized to be the cause of Minamata disease until 1968. **The industrial discharge was stopped at this time, but removing the contamination from the Bay involved a ten-year dredging operation, completed in 1987.**

In 1986 a fire destroyed a chemical store in Basel, Switzerland, near the borders of France and Germany. Chemicals reached the water through the plant's sewage system when **huge amounts of water (10,000-15,000 m³) were used to fight the fire**. The store contained large quantities of 32 different chemicals, including insecticides and raw ingredients, and the water implications were identified through the presence of red dye in one of the substances. The main wave of chemicals destroyed eels and fish, as well as habitats for small animals on the riverbanks. The highest concentration of organic thiophosphates (40 g/l) was 362 km downstream from the fire and the total eel population was destroyed 500 km downstream, from Basel to Loreley. Concentrations of contaminants reached normal values 3 months after the incident. Human health effects were harder to assess, as the potential toxic effects are likely to be long-term and not yet well understood. **As a result of this incident, the permanent chemical load in the Rhine has been reduced and information systems on potential incidents improved.**

FARMEC Company has a range of descalers for toilet. In the past the formulations contained sulphuric acid and hydrochloric acid.

Sulphuric Acid (H₂SO₄) is a highly corrosive strong mineral acid with a pungent-ethereal, colourless to slightly yellow viscous liquid and a reactive and a dangerous chemical. It can cause very severe burns. Inhalation can irritate the nose, throat and lungs. Repeated exposure can cause permanent lung damage, damage to teeth and upset stomach. Acute exposure can cause death. Frequent exposure to big quantities of sulphuric acid may contribute to larynx cancer. Ingestion may cause bleeding, death of tissues and holes in the digestive tract. Contact with skin and eyes may cause burns and eye irritation that can lead to blindness.

Hydrochloric Acid (HCl) is a highly corrosive strong mineral acid, a pungent, clear, colourless liquid and a reactive and a dangerous chemical. It is used in the chemical industry as a chemical reagent in the large-scale production of vinyl chloride for PVC plastic and to produce household cleaning products, different food additives, descaling products and also in leather processing. Concentrated hydrochloric acid (fuming hydrochloric acid) forms acidic mists. It has a corrosive effect on human tissue, with the potential to damage respiratory organs, eyes, skin, and intestines irreversibly.

The care for human health and for the environment, made FARMEC Company, replace these two acids with methane sulfonic acid. Methane sulfonic Acid (MSA) (CH₃SO₃H) is a very strong organic acid, a colourless liquid. It is a biodegradable acid, a less corrosive and less irritant and does not fume.

The benefits provided by MSA in cleaning and descaling products are:

strong acidity -> promotes rapid attack on carbonate and oxide scales

forms highly solubility salts -> enhanced dissolution and removal of salts

non-oxidizing -> minimize degradation of other formulation components

low corrosively to metals vs. other acids -> less damaging to pipes and fixtures

low toxicity and Eco toxicity -> dilute solutions are safe for discharging waste treatment facilities

The most important factor in the design of **carbon fiber** production is at the beginning of the process, the above definitions are from the Atex and HAZOP studies. In accordance with Seveso Directive (Regulations for the Prevention of Major Industrial Accidents) the prevention of accidents and to reduce the risk of any work is done. SEVESO is a city in Italy. **In 1976, It was a major industrial accident and many people died** in this city. The results and lessons learned from this accident created as a result of measures become mandatory regulation. Today, these measures are referred to as **the Seveso Directive**. Industry organizations have to comply with this directive.

Determination of major industrial accidents in organizations is done with quantitative risk assessment methods to assess the risks arising from these hazards. In quantitative risk assessments, which could lead to major accident hazards and the following points are taken into account.

According to this:

- a) The classification of dangerous chemicals and the amounts and interactions of these chemicals
- b) Human exposure to chemicals and / or evaluation from an environmental perspective
- c) Explosive environments and persistence of these environments, explosive atmospheres classification and suitability of equipment to be used in these areas
- d) Process in the determination of dangerous equipment and grouping
- d) Process with the danger of process equipment and / or the interaction of instrument
- e) The reliability of process instruments and emergency shutdown systems assessment and certification
- f) Maintenance and repair of safety data
- g) Reliability-centered maintenance to be carried out and risk-based control methods
- i) Analysis of the root causes and consequences of major accidents scenarios
- h) In the past experienced repeated accidents and quantitative probability of these accidents

i) Human error and reliability analysis in the European Union on the other hand, within the scope of the Seveso II Directive in the organization do they risk assessment “*Identification of possible accident scenarios*” it represents an important element. This with the provider of risk assessment studies on where and how to start, since there are a number of uncertainties regarding how matters will determine the possible accident scenarios and ARAMIS this uncertainty goes to both jointly by member states of the European Union in order to provide guidance to the parties concerned Seveso II Directive in the Context of Industry in Accident Risk Assessment methodology has been developed.

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Organic chemistry

А.В. Великородов, А.Г. Тырков-**ЗЕЛЕНАЯ ХИМИЯ. МЕТОДЫ, РЕАГЕНТЫ И ИННОВАЦИОННЫЕ ТЕХНОЛОГИИ**

Е.С.Локтева, В.В.Лунин- **Прогресс науки и роль «зеленой химии» в современном мире**

Жидкин В.И. Сульдина Т.И. **ЭКОЛОГИЧЕСКИЙ ПОДХОД В ПРЕПОДАВАНИИ ХИМИИ НА ОСНОВЕ ИДЕЙ «ЗЕЛЕННОЙ ХИМИИ»**

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Проф. Мартин Поляков, „**Зелената химия: Следващата промишлена революция ли е?**”

Лекционный курс по дисциплине«**ОРГАНИЧЕСКАЯ ХИМИЯ**»Профессор кафедры химии, доктор химических наук, профессорСахаровИван ЮрьевичДоцент кафедры химии, кандидат химических наукФирсова Юлия Николаевна

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The countries involved:

