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FIELDS OF OZONE APPLICATIONS

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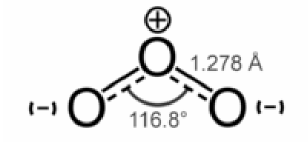
Abstract. The powerful oxidative action of ozone provides basis for development of novel or improved technologies which are widely used in ecology and industry. Special attention is paid to purification of waste gases, water, and soils. The disinfection and cleaning of drinking and process water are considered in detail. Applications of ozone in chemical, pharmaceutical and perfume industries, cosmetics, cellulose, paper and sugar industries, flotation, microelectronics, and many others are also examined in the review.

Key words: ozone, ecology, industry, water, gases, organic synthesis.

1. Introduction

Ozone is a pale blue poisonous gas with a sharp, cold, irritating odor. Most people can detect about 0.01 ppm in air. At 161 K it forms a dark blue liquid. At temperatures below 83 K it forms a violet-black solid. Its molecule contains three oxygen atoms:



has C_{2v} symmetry, O–O bond lengths 1.278 A°, O–O–O angle 116.78^0 and IUPAC name trioxygen.

Ozone forms protective absorbed layer on the altitude of 25–30 km in the atmosphere, where it is synthesized by the reactions:

$O_2 + h\nu = 2\ O$
$O_2 + O = O_3.$
$3O_2 = 2\ O_3$ $\quad \Delta H$ at 101 kPa is +284.5 kJ·mol^{-1}

Sunlight with wavelength until 240 nm brakes the O–O bond in oxygen molecule and forms atomic oxygen, which recombined with a molecule of oxygen forms ozone.

The appeared ozone absorbs the sun light until 320 nm and thereby preserves the life on the earth. The ozone concentration in the ozone layer can reach 50 ppm. The problems with ozone hole are the subject of many special issues but not of this paper.

Exposure to 0.1 to 1 ppm produces headaches, burning eyes, and irritation to the respiratory passages. On the earth ozone is a part of the photochemical smog, and it is produced by photochemical reactions in the air of conifer forests and sea coasts where its concentration varies from 0.005 to 0.05 ppm. In higher concentrations ozone is formed around all devices using radiation from gamma to UV-light and high voltage and sparks.

The allowable ozone concentration in the air of the working places is 0.1 ppm (vol). The olfactory threshold of the ozone concentration is 0.02 ppm (vol).

Ground-level exposure of 0.1 to 1 ppm ozone produces headaches, burning eyes, and irritation to the respiratory passages.

Ozone is not stabile and can not be stored. Its half-life at ordinary temperature in the air is 16–20 h and in water – 15–30 min at solubility of 570 mg/l.

Ozone is a very strong oxidizing agent due to its high oxidation potencial of 2.07 V. By this index it is ordered on the place after fluorine (3.06), hydroxil radicals (2.80), and atomic oxygen (2.42). It oxidizes all metals (except Pt, Au and Ir), non-metals to the highest extents of oxidations, and organic and inorganic compounds in the mild conditions and is extremely activity against viruses, bacterias, microbes, spores, fungi, *etc*. The powerful oxidative characteristics of ozone make it very attractive for industrial usage [1], wide application in ecology [2], chemical, pharmaceutical, and perfume industries, cosmetics [3, 4], cellulose, paper, and sugar industries, flotation, microelectronics, veterinary and human medicine, agriculture, foodstuff industry, and many others [5-8].

The ozone reacts in three ways:

1. Direct oxidation on the substrate by the process of ozonolysis;

2. Direct oxidation on a substrate for the oxygen atom loss;

3. Catalytic oxidation due to the oxygen present in ozonized air.

Corona discharge in a dry process gas containing oxygen is presently the most widely used method of ozone generation for water treatment. A classical production line is composed of the following units: gas source (compressors or liquefied gas), dust filters, gas dryers, ozone generators, contacting units, and off gas destruction.

It is of utmost importance that a dry process gas is applied to the corona discharge. Limiting nitric acid formation is also important in order to protect the generators and to increase the efficiency of the generation process. In normal operation of properly designed systems, a maximum of 3 to 5 g nitric acid is obtained per kilogram ozone produced with air. If increased amounts of water vapor are present, larger quantities of nitrogen oxides are formed when spark discharges occur. Also, hydroxyl radicals are formed, that combine with oxygen radicals as well as ozone. Both reactions reduce the ozone generation efficiency. Consequently, the dryness of the process gas is of relevant importance to obtain a yield of ozone. Moreover, with air, nitrogen oxides can form nitric acid, which can cause corrosion. The presence of organic impurities in the feed gas should be avoided, including impurities arising from engine exhaust, leakages in cooling groups, or leakages in electrode cooling systems.

Oxidation of organic materials by ozone is selective and incomplete at the concentrations and pH values of aqueous ozonation. Unsaturated and aromatic compounds are oxidized and split at the double bonds, producing carboxylic acids and ketones as products. Because of the high reactivity of ozone, oxidation of organic matter in the aqueous environment, whether potable water or wastewater, will consume ozone in varying amounts. Therefore, one of the most significant parameters for evaluating ozone is the determination of the immediate ozone demand. Oxidation of the (organic) material is usually incomplete. It is estimated that the reduction in TOC may be only 10–20 percent although decreases in COD and BOD are generally greater, ranging up to 50 percent of COD reduction.

There are instances where COD has appeared to increase, resulting from conversion to more readily oxidized compounds. Ozone also causes the formation of assimilable organic carbon (AOC). AOCs are compounds that are more readily digested by bacteria.

Ozone is an effective bleaching agent against organic compounds that contribute to color in wastewater and potable water. The ability to attack these compounds, including humates and fulvates, makes ozone a perfect wastewater polishing agent.

The ability of ozone to destroy taste forming phenolic compounds is an important contribution to the field of potable water treatment. Ozone is capable of destroying other taste forming compounds of unknown origin. There are two major mechanisms by which ozone reacts with organic material. The first one is a direct additive attack in which ozonides and ultimately peroxides are formed together with the organic molecule splitting.

Another mechanism is an accompaniment to the decomposition of ozone. This decomposition proceeds by the formation of the free radicals OH, HO_2, and HO_3. These free radicals, especially the hydroxy radical, are highly reactive against organic material and may lead to auto-oxidation of a wide variety of organic matter, particularly substances present in wastewater effluents. The free radical auto-oxidation mechanism may be well involved in the disappearance of residual ozone after the initial rapid demand has been satisfied.

Low levels of ozone have been advertised to be of some disinfectant use in residential homes, however the concentration of ozone in dry air required to have a rapid, substantial effect on airborne pathogens exceeds safe levels recommended by the U.S. Occupational Safety and Health Administration and Environmental Protection Agency. Humidity control can vastly improve both the killing power of the ozone, and the rate at which it decays back to oxygen (more humidity allows more effectiveness). Industrially, ozone is used to:

- disinfect laundry in hospitals, food factories, care homes, *etc.*;
- disinfect water in place of chlorine;
- deodorize air and objects, *e.g.* after a fire; this process is extensively used in fabric restoration;
- kill bacteria on food or on contact surfaces;
- ozone swimming pools and for spas sanitation;
- scrub yeast and mold spores from the air in food processing plants;
- wash fresh fruits and vegetables to kill yeast, mold and bacteria;
- chemically attack contaminants in water (iron, arsenic, hydrogen sulfide, nitrites, and complex organics lumped together as “colour”);
- aid flocculation (agglomeration of molecules, which aids in filtration, where the iron and arsenic are removed);
- manufacture chemical compounds via chemical synthesis [2];
- clean and bleach fabrics (the former use is utilized in fabric restoration) (the latter use is patented);
- assist in processing plastics to allow adhesion of inks;
- age rubber samples to determine the useful life of a batch of rubber;
- clean hospital operating rooms where air and surfaces needs to be sterile;
- eradicate water borne parasites such as *Giardia* and *Cryptosporidium* in surface water treatment plants.

Ozone is a reagent in many organic reactions in the laboratory and in industry. Ozonolysis is the cleavage of an alkene to carbonyl compounds.

Ozone will oxidize metals (except gold, platinum, and iridium) to metals oxides in their highest oxidation state:

$$2\,Cu^{2+} + 2\,H^+ + O_3 \rightarrow 2\,Cu^{3+} + H_2O + O_2$$

Ozone converts oxides to peroxides:

$$SO_2 + O_3 \rightarrow SO_3 + O_2$$

It also oxidizes oxides to oxides of higher oxidation number:

$$NO + O_3 \rightarrow NO_2 + O_2$$

The above reaction is accompanied by chemiluminescence. The NO_2 can be further oxidized:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

The NO_3 formed can react with NO_2 to form N_2O_5:

$$NO_2 + NO_3 \rightarrow N_2O_5$$

Ozone reacts with carbon to form carbon dioxide, even at room temperature:

$$C + 2\,O_3 \rightarrow CO_2 + 2\,O_2$$

Ozone does not react with ammonium salts but it reacts with ammonia to form ammonium nitrate:

$$2\,NH_3 + 4\,O_3 \rightarrow NH_4NO_3 + 4\,O_2 + H_2O$$

Ozone reacts with sulfides to make sulfates:

$$PbS + 4\,O_3 \rightarrow PbSO_4 + 4\,O_2$$

Sulfuric acid can be produced from ozone, either starting from elemental sulfur or from sulfur dioxide:

$$S + H_2O + O_3 \rightarrow H_2SO_4$$
$$3\,SO_2 + 3\,H_2O + O_3 \rightarrow 3\,H_2SO_4$$

All three atoms of ozone may also react, as in the reaction with tin (II) chloride and hydrochloric acid:

$$3\,SnCl_2 + 6\,HCl + O_3 \rightarrow 3\,SnCl_4 + 3\,H_2O$$

In the gas phase, ozone reacts with hydrogen sulfide to form sulfur dioxide:

$$H_2S + O_3 \rightarrow SO_2 + H_2O$$

In an aqueous solution, however, two competing simultaneous reactions occur, one with the formation elemental sulfur, and another with the formation of sulfuric acid:

$$H_2S + O_3 \rightarrow S + O_2 + H_2O$$
$$3\,H_2S + 4\,O_3 \rightarrow 3\,H_2SO_4$$

Iodine perchlorate can be made by treating iodine dissolved in cold anhydrous perchloric acid with ozone:

$$I_2 + 6\,HClO_4 + O_3 \rightarrow 2\,I(ClO_4)_3 + 3\,H_2O$$

Solid nitryl perchlorate can be made from NO_2, ClO_2, and O_3 gases:

$$2\,NO_2 + 2\,ClO_2\ 2\,O_3 \rightarrow 2\,NO_2ClO_4 + O_2$$

Ozone can be used for combustion reactions and combusting gases in ozone provide higher temperatures than combusting in dioxygen (O_2). The following is the carbon subnitride combustion reaction:

$$3\,C_4N_2 + 4\,O_3 \rightarrow 12\,CO + 3\,N_2$$

Ozone can react at cryogenic temperatures. At 77 K atomic hydrogen reacts with liquid ozone to form a hydrogen superoxide radical, which dimerizes [9]:

$$H + O_3 \rightarrow HO_2 + O$$
$$2\,HO_2 \rightarrow H_2O_4$$

Ozonides can be formed, which contain the ozonide anion, O_3^-. These compounds are explosive and must be stored at cryogenic temperatures. Ozonides for all the alkali metals are known. KO_3, RbO_3, and CsO_3 can be prepared from their respective superoxides:

$$KO_2 + O_3 \rightarrow KO_3 + O_2$$

Although KO_3 can be formed as above, it can also be formed from potassium hydroxide and ozone [10]:

$$2\,KOH + 5\,O_3 \rightarrow 2\,KO_3 + 5\,O_2 + H_2O$$

NaO_3 and LiO_3 must be prepared by action of CsO_3 in liquid NH_3 on an ion exchange resin containing Na^+ or Li^+ ions [11]:

$$CsO_3 + Na^+ \rightarrow Cs^+ + NaO_3$$

Treatment of calcium dissolved in ammonia with ozone leads to ammonium ozonide not calcium ozonide [12]:

$$3\,Ca + 10\,NH_3 + 6\,O_3 \rightarrow Ca{\bullet}6NH_3 + Ca(OH)_2 + Ca(NO_3)_2 + 2\,NH_4O_3 + 2\,O_2 + H_2$$

Ozone can be used to remove manganese from water, forming a precipitate which can be filtered:

$$2\,Mn^{2+} + 2\,O_3 + 4\,H_2O \rightarrow 2\,MnO(OH)_{2\,(s)} + 2\,O_2 + 4\,H^+$$

Ozone will also turn cyanides to one thousand times less toxic cyanates:

$$CN^- + O_3 \rightarrow CNO^- + O_2$$

Finally, ozone will also completely decompose urea [13]:

$$(NH_2)_2CO + O_3 \rightarrow N_2 + CO_2 + 2\,H_2O$$

2. Ecology

2.1. Waste Gases

More than 100 contaminants of the atmospheric air have been identified. Among them SO_2, CO_2, nitrogen oxides, various hydrocarbons, and dust constitute 85 %.

The main sources of harmful substances emissions, *i.e.* dust, SO_2, and CO_2 in the air are coke, briquettes, and coals processing plants, thermal power stations, air, water, and road transport [9].The exhaust gases contain also CO, organic and inorganic compounds, *etc.* [10]. Dust, sulfur dioxide, carbon dioxide, nitrogen oxides, and organic compounds, *etc.* are the main pollutants released in the environment from metallurgy, fertilizers industry, and petrochemistry. The most typical air pollutants emitted by some chemical productions are listed in Table 1.

The technologies with ozone participation are very promising for SO_2 utilization as sulfate, CO as carbonate, and nitrogen oxides as nitrates.

Scrubbers used previously for removing only acids, for example HCl and HF *etc.*, now can be used for SO_2

Table 1

Main air contaminants emitted by chemical productions

No.	Production	Pollutants	No.	Production	Pollutants
1.	Nitric acid	NO, NO_x, NH_3	12.	Ammonium nitrate	CO NH_3, HNO_2, NH_4NO_3 – dust
2.	Sulfuric acid: a) Nitroso b) contact	NO, NO_x, SO_x, H_2SO_4, Fe_2O_3, dust	13.	Superphosphate	H_2SO_4, HF, dust
3.	Hydrochloric acid	HCl, Cl_2	14.	Ammonia	NH_3, CO
4.	Ocsalic acid	NO, NO_x, $C_2H_2O_2$, dust	15.	Calcium chloride	HCl, H_2SO_4, dust
5.	Sulfamidic acid	NH_3, H_2SO_4, $NH(SO_3NH_4)_2$,	16.	Chlor	HCl, Cl_2, Hg
6.	Phosphor	P_2O_3, H_3PO_4, HF, $Ca_5F_4(PO_4)_2$, dust	17.	Caprolactam	NO, NO_2, SO_2, H_2S, CO
7.	Phosphoric acid	P_2O_3, H_3PO_4, HF, $Ca_5F_4(PO_4)_2$, dust	18.	PVC	Hg, $HgCl_2$, NH_3
8.	Acetic acid	CH_3CHO, CH_3OH	19.	Artificial fibers	H_2S, CS_2
9.	Nitrogen fertilizers	NO_2, NO, NH_3, HF, H_2SO_4, HNO_3	20.	Mineral pigments	Fe_2O_3, $FeSO_4$
10.	Carbamide	NH_3, CO, $(NH_2)_2CO$, dust	21.	Electrolysis of NaCl	Cl_2, NaOH

separation via the addition of an oxidizing agent into the water intended for gas treatment.

Ozone as compared with the conventional oxidizers such as hydroperoxide, chlorine, sodium hypochloride, perchlorate, shows appreciably higher oxidizing efficiency [11].

The rate constant of ozone reaction with NO is about 1010 cm^3/(mol·s), and with NO_2 it is ~ 107 cm^3/(mol·s) whereby the oxidation of NO by ozone in the liquid phase is characterized by a higher absorption rate and rise in the concentration of the obtained HNO_3. Moreover the oxidation of NO can be accomplished in the exhaust gases or in the course of absorption [12].

The CO oxidation by ozone is carried out in the presence of Fe, Ni, Co, and Mn oxides. In most cases ozonation is more appropriate than the conventional methods and sometimes it appears the only possible way for its preparation [13].

The purification of exhaust gases from burners working on liquid and gas fuel is accomplished by using oxidation catalysts of ABO3 perovskite-type oxides combined with ozonation. Ozone is injected prior to the waste gases flow. A may be La, Pr, or other alkali earth element; B may be Co, Mn, or other transition metal. A may be also partially substituted by Sr, Ca, or any other alkali earth element. A catalyst deposited on ceramic support of honeycomb type may contain $SrCo_{0.3}Mn_{0.7}O_3$. It is oxidized 24 % CO in the absence of ozone and 80 % in ozone atmosphere [14].

The removal of nitrogen oxides (NO_x) from waste gases is carried out through ozone oxidation in a charged vertical column. The lower part of the column is loaded by 5–15 % $KMnO_4$, and ozone is blown through the lower and upper part of the column and the waste gases are fed to the center of the column charge. The inlet concentration of 1000 ppm NO_x in the waste gas is reduced to 50 ppm in the outlet gas flow. Another method for cleaning of exhaust gases from NO_x involves the application of plasma generator and ozonator [15] which practically leads to the complete removal of nitrogen oxides.

Sulfur containing compounds are removed from gas mixtures by silicon oil scrubbing and ozone oxidation of absorbed pollutants. A model system providing that the gas mixture contains methandiol and deimethylsulphide is fed at a rate of 9–120 m^3/h into silicon oil charged scrubber followed by ozone oxidation of the absorbate. The oxidates are extracted with water and the silicon oil is regenerated. Thus the purified gas mixtures practically do not contain any sulfur [16].

A special apparatus is designed for decomposing acyclic halogenated hydrocarbons in gases. It includes a chamber for mixing of the waste gases with ozone coupled with UV-radiation, ozonator, and inlet and outlet units. This method is very appropriate for application in semiconducting industry whereby acyclic and halogenated hydrocarbons are used as cleaning agents [17].

The mechanisms of ozonolysis of volatile organic compounds such as alkenes and dienes are discussed and the products output is determined by matrix isolation FT-IR spectroscopy [18].

The synthesis of a material from zeolite via pulverization, granulation, and drying at 773–973 K, cooling to 373–473 K, electromagnetic radiation or ozone treatment is described in [19]. The material obtained is suitable for air deodorization, drying and sterilization.

The purification of gases containing condensable organic pollutants can be carried out by gas treatment with finely dispersed carbon, TiO_2, Al_2O_3, Fe_2O_3, SiO_2 and H_2O_2 and ozone as oxidizers [20].

A wet-scrubbing process for removing total reduced sulfur compounds such as H_2S and mercaptans, as well as the accompanying paramagnetic particles from industrial waste gases is proposed [21]. For this purpose a water-absorbing clay containing MnO_2 is used. The collected clay is regenerated by ozone oxidation.

The removal of mercury from waste gases is carried out by catalytic ozonation [22]. The used gases mixed with ozone are blown over a zeolite supported Ni/NiO catalyst. This procedure results in 87 % conversion of mercury into mercuric oxide which is isolated by filtration. Pt and CuO_x/HgO system is proposed as another catalyst for this process [22].

2.2. Waste Water

In contrast to the cleaning of natural water by ozonation, which is experimentally confirmed as the most appropriate, the purification of waste water by ozone is still an area of intensive future research. This could be explained by the great diversity of pollutants in the used water and the necessity of specific approach for each definite case.

The recycling of water from cyanide waste water (copper cyanide contaminant) is accomplished by ozone oxidation combined with UV radiation and ion exchange method [23]. Further, the oxidate is passed through two consecutive columns charged with cationite and anionite resins. The ozonolysis priority over the conventional chlorinating method is demonstrated by the fact that ozonation fails to yield chlorides whose removal requires additional treatment.

The ozonolysis of CN ions leading to CNO^- ion formation combined with UV-radiation proceeds at threefold higher rate as compared with that without radiation employment. Upon exchange in NaOCN, the Na^+ is substituted by H^+ followed by its decomposition to CO_2 and NH^{4+} via hydrolysis in acid medium. The ammonium ion is absorbed by the cation-exchange resin. The solution electroconductivity on the anion-exchange resin becomes lower than 10 mu·S/cm and cyanides, cyanates or copper ions have not been monitored. On the basis of these experimental results, a recycling method and apparatus for detoxification of solutions containing cyanides is proposed. The recycled water from the cyanide waste water may be re-used as deionization water in gold-plating. The process ion-exchange resins are regenerated after conventional methods. Actually, this method is not accompanied by the formation of any solid pollutants [23].

The waste water from the electrostatic and galvanic coatings containing CN^- -ions and heavy metals is treated consecutively by ozone and CO_2. The cyanides and carbonates accumulated in the precipitate are already biodegradable [24].

Waste water containing Cr(III) is oxidized by ozone combined with UV-radiation [25]. The radiation reduces the oxidation time about three-fold. The oxidate is consecutively passed through columns charged with cationite and anionite resulting in the obtaining of waste water with electroconductivity below 20 mu·S/cm. This deionized water can be successfully used for washing of coated articles. The Cr(IV) concentrated solution from the anionite regeneration can be further treated by appropriate ion-exchange method yielding a high purity Cr(IV) solution [25].

Purification of waste water containing $ClCH_2COOH$ and phenol is carried out by ozone treatment and UV-radiation in the presence of immobilized photocatalyst. Thus the rate of decomposition is higher than the rate obtained only in the presence of ozone and UV-radiation [26].

Used water containing small amounts of propyleneglycol nitrate or nitrotoluenes is a subject to combined oxidation with ozone and H_2O_2, under pressure and heating to the supercritical point. Thus a nominal conversion of the contaminants higher than 96.7 % is achieved [27].

In laboratory experiments for reduction in residual COD in biologically treated paper mill effluents it is subject to ozonation or combined ozonation and UV radiation at various temperatures and pressures [28]. At a ratio of the absorbed ozone to COD less than 2.5:1 g/g, the elimination level with respect to COD and DOC is up to 82 % and 64 %, respectively. The ozone consumption is essentially higher in the case of the UV combined ozonation at pH>9 and elevated temperature to 313 K.

The decolourization and destruction of waste water containing surface active substances is performed by ozone treatment at ozone concentration of about 80 mg/l. It has been found that for waste water which has undergone partial biological treatment by fluent filters or anaerobe stages up to COD concentration > 500 mg/l and ratio 30D5/COD>0.2 ozonolysis with ozone concentrations up to 1.8 g/l does not change CBR, while after the complete biological treatment at COD<500 mg/l ozonation results in the rise of the 30D5/COD ratio from <0.05 to 0.37. This evidences the increase of CBR [28].

The purification of waste water from paper manufacture characterized by enhanced biodegradability, as well as the removal of COD and halogenated compounds is carried out by a method based on ozonation and biofiltration [29].

Waste water from the paper pulp production is cleaned up by the treatment with ozone and activated acid tar. The high values of pH favor the lignin decomposition and carboxylic acids formation since in this case the •OH – radicals and not ozone are the oxidizing agent. The application of activated acid tar has a positive effect on the dynamics of the microbiological growth, substrate consumption, and CBR of organic acids. For example, maleic and oxalic acids are decomposed completely at ozonation of waste water in the presence of activated acid tar. For immobilization of biological culture the use of polyurethane foams appear to be very suitable [30].

The used water in collectors of a plant for paper manufacture is ozonized in a foamy barbotating contactor. The results indicate that ozone is very efficient in the oxidation of coloring and halogenated compounds. Its activity is proportional to the amount of absorbed ozone regardless of the variations in the gas flow rate, the inlet ozone concentration and contactor design. The amount of consumed ozone depends on the operating conditions and waste water characteristics. The absorption rate rises in the presence of stages including ozone decomposition, particularly at higher rates [31].

In biological granular activated carbon (GAC) columns the effect of pretreated ozonation on the biodegradability of atrazine is investigated. The metabolism of isopropyl-^{14}C-atrazine gives higher amount of $^{14}CO_2$ than the ring UL-^{14}C – atrazine which shows higher rate of dealkylation than the process of ring cleavage. The pretreatment with ozone increases the mineralization of the ring UL-^{14}C – atrazine and consequently raises the GAC-columns capacity. 62 % of the inlet atrazine is transformed into $^{14}CO_2$ in columns charged by ozonized atrazine and water. However, in columns with nonozonized atrazine and water only 50 % of the inlet atrazine is converted into $^{14}CO_2$ and in columns supplied only with nonozonized atrazine only 38 % of it are converted to $^{14}CO_2$ [32].

The waste water from petrochemical industry contains substantial amounts of phenol. The phenols mixtures appear to be more toxic than phenol itself and possess a synergetic effect. Their decomposition to nontoxic products is an acute problem. The oxidation of phenols such as *p*-cresol, pyrocatechin, rezorzine, and hydroquinone by O_3 in aqueous medium appears to be a promising method for their degradation. At concentrations of 100 mg/l and pH = 11.5 their complete oxidation is performed for 30 min.

The phenol content in used water is reduced from 145–706 mg/l to 2.5 mg/l at ozone consumption of 1.1–2.6 g/l. In real conditions the ozone consumption varies from 5 to 10 g/l per g phenol (Table 2).

The treatment of concentrated aqueous solutions of phenol (1.0 g/l) with ozone causes the appearance of a yellowish coloring after absorption of 1 mol O_3 per 1 mol phenol which gradually fades away. In this case the higher phenols undergo slight oxidation and H_2O_2 is identified in the water after the treatment.

Table 2

Results of the ozonation of waste water from coke processing. [O_3] = 5 mg/l, flow rate 6 l/min and treatment time – 4 h

Pollutant, mg/l	Before ozonation	After ozonation
Monophenols	710	0.8
Polyphenols	380	198
Cyanides	3	29
Thiocyanides	384	0
Thiosulfates	538	0
Sulfides	43	2
H_2O_2	0	12
Bases	114	27

The tests demonstrate that upon varying content of phenols in the used water the ozonation is one of the most promising method for their removal. The ozonation was found to be applicable for the decomposition of rhodanide in neutral and weak acid medium in the temperature range of 282–298 K. The ozone consumption in this case is 2 mg/mg. The ozone uptake for the oxidation of the cyanide ion (CN^-) is 1.8 mg/mg.

The complex Zn cyanides are oxidized similarly to the simple soluble cyanides. Regardless of the higher resistance of Cu cyanide complexes, the ozone treatment reduces the CN^- content substantially (traces). Copper carbonate is precipitated as a reaction product.

The ozonation can be successfully employed as a method for cleaning the waste water from the manufacture of ammonium nitrate containing CN^-, S^{-2}, CSN^- ions. The purification levels are 83, 98, and 95 % respectively at O_3 consumption of 0.7 g/l/g water for 10 min contact.

The ozonation of waste water from sulfate-cellulose production results in 60 % purified used water which is returned in the process cycle.

The cleaning of waste water from the petrochemical plants by ozone is efficient under wide range of pH (5.8–8.7) and temperatures (278–323 K). Thus the level of petrochemicals in the waste water at pH 5.8, ozone consumption of 0.52 mg/mg and 10 min contact is reduced from 19–33 mg/l to 2 mg/l. In Table 3 the efficiency of various treatment procedures for deodorization of petrochemicals contaminated water is shown.

Ozonation is a very economical and highly efficient method for decomposing carcinogenic substances such as 3,4-benzopyrene *etc*., particularly after the biological purification of waste water.

The application of ozone is also advisable for mercury oxidation in chlorine producing, for decontamination of the used water from the poisonous tetraethyllead, for destroying pesticides traces, *etc*.

The highest efficiency of cleaning of petrochemicals contaminated water is achieved at the following sequence: primary cleaning (mechanical),

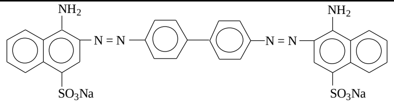
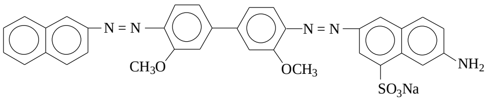
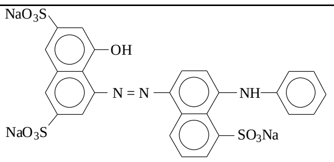
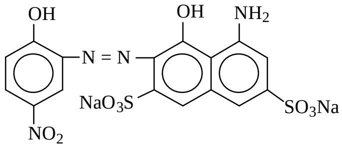
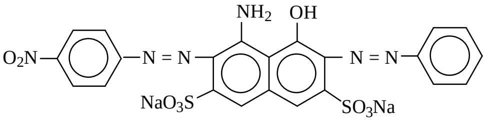
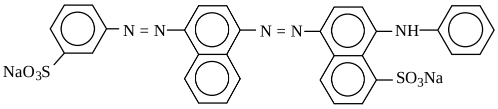
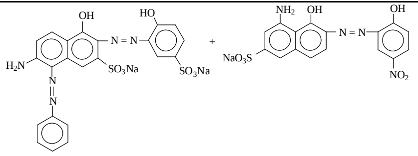
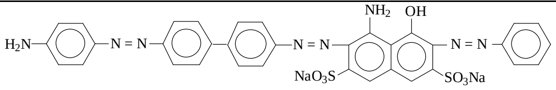
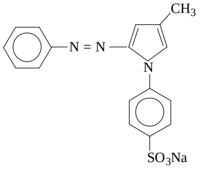
Table 3

Petrochemicals contaminated water deodorization results (grades/dilution)

Petroleum products	Before treatment	Coagulation and filtration	Charcoal and filtration	Chlorination	Ozonoation	Coagulation, filtration and ozonation
Petrol	5/80	5/60	5/50	5/80	2–3/10	1/0
Kerosin	5/100	5/80	5/70	5/100	4–5/25	1/0
Petroleum	5/100	5/60	5/60	5/100	5/20	2/5
Oil	5/10	1/0	1/0	5/10	1–2/2	1–0/0

Table 4

Ozonated dyes at the Kostenetz plant

Order number	Dye's name	Empiric formula	Molecular weight	Structural formula
1.	Direct Congo red	$C_{32}H_{26}O_6N_6S_2Na_2$	698	
2.	Direct blue KM	$C_{34}H_{30}O_5N_5S_1Na_1$	643	
3.	Acid blue ZK	$C_{26}H_{20}O_{10}N_3S_3Na_3$	699	
4.	Acid chromium green	$C_{16}H_{11}O_{10}N_4S_2Na_2$	529	
5.	Acid black ATT	$C_{22}H_{16}O_9N_6S_2Na_2$	618	
6.	Acid sulfonic blue	$C_{32}H_{25}O_6N_5S_2Na_2$	685	
7.	Acid chromium black C	$C_{22}H_{19}O_5N_6S_1Na_1$ + $C_{16}H_{13}O_7N_4S_1Na_1$	502 428	
8.	Direct black Z	$C_{34}H_{26}O_7N_8S_2Na_2$	768	
9.	Acid chromium yellow R	$C_{17}H_{14}O_3N_3S_1Na_1$	367	

secondary (biological), and complete purification (ozonation).

Ozone is also successfully applied for the complete purification of waste water from dyes manufacture. Their color decreases about 10 000 times at exposure to 0.22 g/l ozone and the biological activity of the reaction products is reduced almost to zero. The semi-industrial experiments at the chemical plant ”Kostenetz” (Bulgaria) were carried out on the dyes manufactured at the plant (Table 4).

In the process of developing a technology for water purification from various organic contaminants, we have proposed a method and apparatus for quantitative determination of chemical compounds, separated by means of liquid chromatography. Special attention is paid to those compounds susceptible to ozone attack such as olefin hydrocarbons and their derivatives, phenols, amines, thiocarbamates, inorganic compounds, *etc*. The characterization of the separated compounds is carried out by spectral, mass spectral, refractometer, electrochemical analyses, but the detectors in most of these equipments are rather expensive and complex units without sufficient identification capabilities, particularly for the compounds pointed above. In this sense the apparatus designed by us allows to overcome the disadvantages of the known methods and equipments. The scheme of the ozone detector applicable for identification and liquid chromatography separation of chemical compounds is presented in Fig.1.

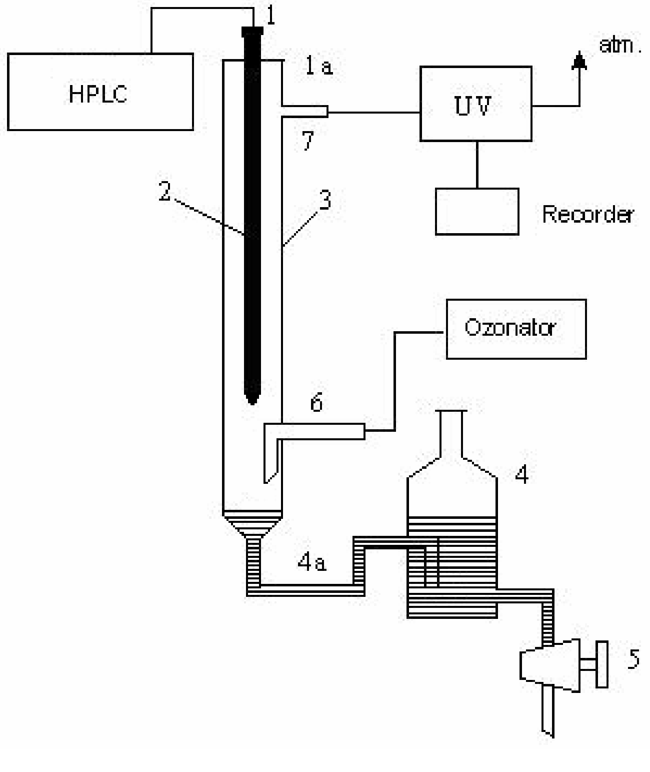


Fig. 1. Set-up of ozone detector for identification of chemical compounds separated by liquid chromatography: eluent access (1); entry for pouring out the elate as thin film (1a) on solid glass stick (2); outer glass jacket (3); vessel for eluent accumulation (4); hydraulic detente (4a); tap for pouring out the eluate (5); ozone inlet (6) and ozone outlet (7)

The ocean power stations operate on the basis of the temperature difference between the upper and lower water layers. Taking advantage of the one-step solution of ozone in depth, the COD is decreased, which prevents the befouling in the piping systems found in the upper layers. The ozone-enriched water from the lower layers is supplied to a cyclic filter and is directly injected into upper seawater for control of the sea microorganisms’ growth [33].

The removal of benzofurenes from ash, clays, soils, water, and oils by combustion, ozonolysis of supercritical water, cracking-processes of petroleum, as well as thermal, photochemical, and biological decomposition have been the subject of many investigations [34]. The direct blowing of ozone through water pipers results in slimes removal from the inner pipers’ walls [35].

The principal mechanism of advanced oxidation processes (AOPs) function is the generation of highly reactive hydroxy-radicals. Consequently, combination of two or more AOPs expectedly enhances free radical generation, which leads to higher oxidation rates [36]. Among various wastewater treatment options ozone-based AOPs such as ozone/H_2O_2, ozone/UV and ozone/H_2O_2/UV are key technologies for degrading and detoxifying of all major groups of pesticides, namely carbamates, chlorophenoxy compounds, organochlorines, organophosphates, aniline-based compounds, pyridines and pyrimidines, triazines, and substituted ureas [37, 38]. AOPs and ozonation are also promising for efficient degradation of pharmaceuticals in wastewater [39].

Photocatalytic oxidation and ozonation appear to be among the most popular treatment technologies for the wastewater compared with other (AOPs) as shown by a large amount of information available in the literature [40]. Photocatalytic oxidation and ozonation is a promising way to perform the mineralization of the wastewater substances like organohalogens, nitrocompounds, organic pesticides and insecticides, surfactants, and colouring matters [41-43].

The ozone blowing at a rate of 2.87 mg/min through aqueous solutions of 15 pesticides with 10 μg/l concentration leads to their transformation and their concentrations are reduced by about 20 % for 60 min. The identified intermediates from the rearrangement of EPN, phenitrothione, malathion, diazinon, izoxathion and chloropiriphos are the corresponding oxones, while for phenthione they are the corresponding sulfoxide, sulfone and sulfooxide oxone analogues, and for disulfothione the intermediate is its sulfo analogue. 2-Amino-4-ethylamino-6-chloro-1,3,5-thriazine is identified as symazin and its

4-isopropylammonium derivative is atrazine intermediate. The isopropylthiolane results in obtaining of its 1-oxo-derivative. Upon replacement of ozone by air practically no changes are registered [44].

At the purification of process water containing pesticides in a soil decontamination plant the removal of organophosphorous compounds such as Thiometon and Disulphoton is of particular importance. In this connection four methods have been applied: 1) ozonolysis at pH = 2.5; 2) ozonolysis at pH = 8; 3) UV/H_2O_2 treatment and 4) oxidation by Fenton reagent [45]. The laboratory experiments were carried out with pure compounds soluted in buffered deoionized water and in process water which is extracted by solid-liquid extraction of the contaminated soil. The use of ozone in an acid medium turns to be ineffective since the Thimeton reaction practically stops after the formation of PO-derivatives. In all cases when the oxidation is carried out by HO – radicals, a sufficient removal of the pesticides and their metabolites is achieved. Oxadixyl, a cyclic nitrogen containing compound which is present in high concentrations in the process water is the most stable one, thus being the main soil contaminant. The investigated experimental conditions and the results obtained show that these methods are quite acceptable for universal application [45].

The water-soluble agrochemicals ASULAM and MECOPROP are decomposed for 30 min at ozone blowing (flow rate – 5.1 mg/min and concentration of 10 ppm) through their aqueous solution (200 ml). The decrease in the flow rate of ozone retards the decomposition process. Similar treatments for 5h give in ACEPHATE and DICAMBA decomposition to 20 %, the rate of decomposition being promoted with H_2O_2 addition [46].

The primary ozonation products of organophosphorous pesticides in water such as diazinone, phenthione (MPP) and ediphenphos (EDDP) [47] are identified by means of GC-MS analysis. The mass spectra of the ozonation products of 17 organophosphorous pesticides point oxones as the primary reaction products. This fact is also confirmed by the SO_4^{2-} generation resulting from the ozonation of their thiophosphoryl bonds. Oxones are relatively stable towards ozone attack but they are further hydrolyzed to trialkylphosphate and other hydrolysis products. However, with MPP the thiomethyl radicals are first oxidized to thiophosphoryl bonds and MPP-sulfoxide, MPP-sulfone, MPP-sulfoxide-oxone are obtained. Two main oxidation products have been identified at the oxidation of bis-dithio-type ethiones. Phosphate type EDDP is stable towards ozonolysis but its oxidation products are identified after hydrolysis [47].

Pesticides and their degradation products which are not mineralized to CO_2, NH_3, H_2O and inorganic salts can damage and contaminate the water piping. The treatment by photolysis or ozonation may substantially increase the mineralization rate. The photodestructive products of S-triazoles, chloroacetanylide and parakaute are dechlorinated and/or oxidized. The ozonation of these herbicides results in formation of products whose side alkyl chains are oxidized or removed, and the aromatic ring is oxidized or soluted but dechlorination does not occur. In some cases the medium may cause microbiological effect [48].

A deodorization method for treatment of ill-smelling air containing ammonia, hydrogen sulfide, or amines from refrigerator chambers, lavatories, cattle-sheds, etc. involves the ozone contact with air in the presence of porous catalyst of 120 m^2/g specific surface. The used gas passes through a layer of carbon black for adsorption of the residual ozone and the nondegradated smelling substances. The active component of the catalyst may be transition metal or its oxides supported on porous honeycomb type supports [49].

The contaminated smelling gases in drain and fecal water are dried to 60–30 % humidity, followed by ozone treatment on an oxidizing catalyst. For example, contaminated gas containing 30 ppm methylsulfide is dried to 30 % humidity and then is treated with ozone in the presence of honeycomb type catalyst containing 83:12.5= = $TiO_2:SiO_2:MnO_2$ with a volume rate of 50 000 h^{-1}. In this case the deodorization efficiency is 99 % while at 100 % humidity it drops to 80 % [50].

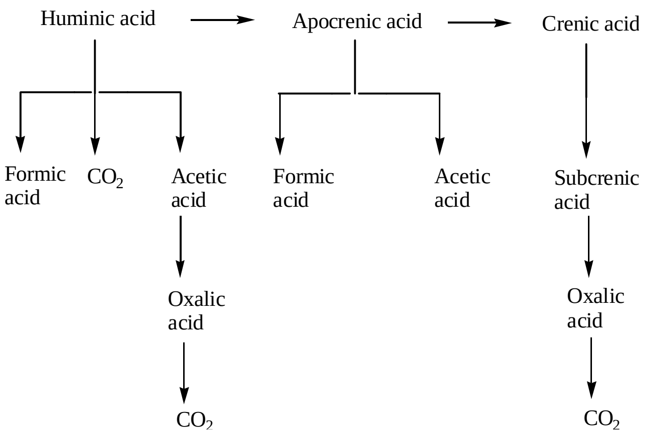
2.3. Natural (Drinking) Water

The basic sources of drinking water usually contain various organic admixtures (in mg/l): carbon – 30, nitrogen – 0.8, fatty acids – 30, highmolecular organic acids – 0.2, naphthenolic acids – 1.5, phenols – 1.2, luminescent substances: neutral resins – 17 %, oils, humus – 55 %, acid resins – 19 %, hydrocarbons, naphthenolic acids – 4–7 % [51].

The coloring of natural water varying from pale yellow to brown is due to the presence of humus substances, Their decolorization is carried out by adsorption on coagulated $Al(OH)_3$ or $Fe(OH)_3$. The increasing demand for fresh water requires the use of more colored water which however is pre-chlorinated and then subject to adsorption up to their complete decolorization [52].

The ozone treatment removes the bad taste and odor of water, the resistant phytoplankton being oxidized to 20 %. The ozone consumption for decolorization of natural water varies in broad limits – from 1 to 18 mg/l and depends on the humus composition [51]. The process of humus compounds oxidation by ozone is presented in Scheme 1.

The various biological processes lead to formation of substances causing the bad taste and smell of water – mercaptanes, sulfides, alcohols, carbonyl compounds, acids, terpenes, amines, *etc*. The deodorization effect of



Scheme 1

Table 5

Some of the world's biggest ozonation stations for drinking water treatment

City	State	Water, m^3/day	Ozone, kg/h
Moscow	Russia	1 200 000	200
Montreal	Canada	1 200 000	150
Ashford Common	GB	-	146
Coppermills	GB	-	144
Neuilly-sur-Marne	France	600 000	120
Choisy-le-Roi	France	900 000	120
Masan	Korea	-	112.5
Kiev	Ukrain	400 000	80
Helsinki	Finland	495 000	63
Manchester	GB	480 000	50
Orly	France	320 000	50
Singapore	Singapore	230 000	48
Minsk	Belaruss	200 000	47
Mery-sur-Oise	France	300 000	45
Lodz	Poland	190 000	40
Chiba	Japan	270 000	38
Nizhni Novgord	Russia	350 000	30
Bodenzee	Germany	480 000	30
Nant	France	380 000	30
Amsterdam	Holland	125 000	25
Brussels	Belgium	250 000	24
Quebec	Canada	220 000	19
Wrotzlaw	Poland	180 000	17

ozone is preserved in wide range of pH values, temperatures, and ion composition. Due to its high oxidation potential, ozone can also degrade the resistant toxic substances. It is known that during blooming in water reservoirs biologically active substances are accumulated, among which algotoxine is particularly harmful to human health. Its complete degradation is achieved by using ozone concentration of 14 mg/l and 50 min contact time [53].

At ozone concentration of 8 mg/l in water, only 6 % of *Scendezmus* algae remain alive after 10–15 min. However it should be noted that the ozone action on the various algae is quite different and specific. Thus *Astetionella* type algae are highly ozone resistant [52].

The oxidative, disinfective, decolorizative and deodorizative properties of ozone have found wide application for preparation of drinking water [54, 55]. Many world corporations such as the French Taileygas, Degramont, Ozonia, the German Fisher, AEG, Siemens, the Swiss Braun & Bovery, the American General Electrics, General Motors *etc*., are among the biggest producers of drinking water [56]. Twenty of the biggest world ozonation stations for drinking water treatment are listed below (Table 5).

Ozonation stations for drinking water preparation work all over the world: in Portugal, Greece, Bulgaria, USA, *etc*.

The technology of drinking water ozonolysis leading to its deodorization, disinfecting, and decolorization includes gas units for dry air producing, ozonator, barbators or other mixing units, apparatus for HO•-radicals generation, promoting the ozone formation and filter-catalyst for decomposition of the residual ozone [57]. The preferable materials for barbators are zeolites or ceramics on the base of aluminum and/or silicon with pores diameter of 5–100E, and the catalysts should contain one or several of the following components: Pt, MnO_2, CuO, Ni_2O_3, Zn, YiO_2 and SiO_2 [58].

For disinfection of drinking water, the ozone-containing air is mixed with water in the water pipe, after which the bubbled water is supplied into a special designed chamber filled by porous ceramics charge for intensification of ozone dissolution into water. Some problems concerning the optimization of the UV stimulated oxidation of organic contaminants in soil water with ozone and hydroperoxide are discussed [59].

The disinfection of drinking water by ozonation can be also carried out at the outlet of various water supplying units before and after consummation, such as taps, fountains, water heaters, dental units [60], *etc*. In this connection small dimensional and low capacity personal ozonators coupled or installed additionally to the above equipments are used.

The attempts for treatment of drinking water with ionization radiation appear to be ineffective mainly because of nitrates and H_2O_2 formation. These problems, however, do not occur when the radiation is performed in the presence of sufficient ozone amount [61]. The addition of ozone before and in the course of radiation converts the radiation into a purely oxidation process, a modification of the so called – Advanced Oxidation Process (AOP). The combined ozone-ionization radiation method is unique since two processes for HO radicals generation are simultaneously induced. This method yields higher concentrations of HO radicals as compared with other AOPs. This in turn results in precipitation of smaller amounts at equal ozone concentrations or reduces the ozone consumption at the same amount of precipitates. This makes the process particularly suitable for remediation of weakly contaminated soil water. The ozone concentrations in this process are higher than those used for drinking water disinfection. Thus, the drinking water treated in this way is disinfected more rapidly. The purification of waste water using this method is more efficient than the UV-radiation treatment only. This combination reduces COD without causing the rise of BOD. In this sense this method appears to be more attractive than the conventional two-stage processes of ozonation and biological treatment. The injection of gaseous ozone into the radiation chamber improves the water flow turbulence and substantially increases the efficiency of contaminants degradation.

The European organization "European regulation" has approved the use of ozone for iron and manganese removal from mineral water, thereby initiating the studies on the secondary products formation, amount, and composition, particularly during ozonation of bromine water. This water usually contains BrO_3^- ions and various halogenated organic compounds (HOC). For some projects admissible concentration limit (ACL) of HOC is 25 μg/l BrO_3^--ions, while after other it is from 10 to 0.5 μg/l. The present standard for LD of HOC is 100 μg/l [62]. Upon ozonation of bicarbonate mineral waters – sodium-rich water and calcium rich water it has been established that: 1) the process depends on the initial Fe and Mn concentrations and Na and Ca concentrations; 2) HOC and bromate ions are secondary products and 3) the specific components characterizing a definite mineral water affect the ozonolysis. This requires definition of the conditions for Fe and Mn removal for each concrete type of mineral water. The removal of iron and manganese is efficient when the amount of ozone is three times greater than the stoichiometric one (0.43 mg O_3/mg Fe and 0.87 mg O_3/mg Mn).

The disinfection of swimming pool water is carried out by controlled addition of the compounds – bromine and iodine donors (NaBr or NaI) and water oxidation by hypochloride, ozone or potassium peroxymonosulfate [63]. We have designed a compact module system (stationary and mobile), which includes module for air preparation, ozonator, absorption column, and unit for the complete decomposition of the residual ozone. Its capacity is 12–15 g/h and it is very suitable for sanitation of drinking water and used water from swimming pools (3.5 l/s capacity).

2.4. Soils

The decontamination of dredging wastes containing spilled petroleum is carried out by using a system for the direct injection of ozone (100–1000 ppm) containing air into pipes at the bottom; means for pumping out the spilled petroleum to a tank for its storage; units for its mixing with ozone for decomposition of organic matter in the tank; units for returning of the processed petroleum for the complete degradation of the residual organic matter by aerobic bacteria. The efficiency of organic matter decomposition is about 20 % higher than the conventional methods including only treatment by ozone [64].

Another technology of contaminated soils treatment [65] involves the ozonolysis of the water slurry of the contaminated soil layer in the presence of H_2O_2 or in its absence and consecutive biological decomposition. The priority of the proposed technology over the conventional ones is that the removal of organic contaminants implies *on-site* treatment of the soils.

The *on-site* recyclation of petroleum contaminated soils by ozonation requires the good knowledge of the geological setting and the recycling system. Usually the recycling stages include: 1) system for air evacuation from the soil; 2) means for injection of ozone combined with air evacuation from the soil; 3) development of means for ozone generation; 4) screening of soils contaminants; 5) use of safety control systems; 6) organization of the cleaning units – pumping and injecting drills; 7) decision for air injection into the soil; 8) methodology for measurement and regulation of ozone concentration; 9) hydraulic purification of the highly contaminated soil areas, *etc*. [66].

The treatment by ozone can be successfully applied for decomposing mineral oils, polycyclic aromatic compounds (PACs), phenols, and some pesticides to biodegradable nontoxic compounds. It should be noted that although ozone decomposes a great number of microorganisms – the soil microflora – can be easily remediated after this treatment [67]. The latter can be carried out on- and out of the contaminated area. A number of problems related to the ozonolysis of organic compounds, the PACs degradation products, the effect of ozone on the soil microflora, the laboratory and pilot results, *etc*. are discussed.

A method and apparatus for decontamination of wastes such as soil, porous granulated sludge, are suggested. The polluted materials are placed in a special vessel and ozone is bubbled through. The waste gases obtained from the ozone oxidation are further treated with ozone [68].

Both methods for ozone treatment (*in-situ* and *on-site*) have appeared to be applicable for the degradation of organic substances adsorbed on the solid surface [69].

Wet-scrubber method (based on MnO_2) for removing total reduced S-containing compounds such as H_2S, mercaptanes, and non-magnetic particles from industrial waste gases using ozone is suggested [21].

3. Industry

3.1. Manufacture of Organic Compounds

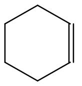
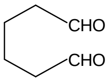
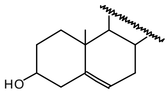
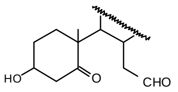
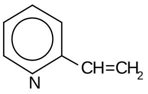
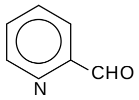
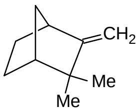
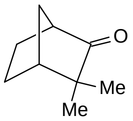
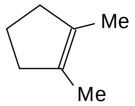
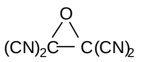
We will focus our attention on some of the numerous ozone applications in organic polymer and inorganic productions, passivation, cleanup, and preparation of surfaces for electronics, superconductors, *etc*.

The reaction of ozone with olefins is the main reaction for ozonides preparation (1, 2, 4-trioxalanes) which can be converted into a mixture of carbonyl compounds, the exact composition of which depends on the olefin structure. This reaction is used for synthetic purposes as with small exceptions the C=C bond is cleaved quantitatively under very mild conditions. Usually the ozonolysis is carried out at low temperatures (as a rule at 203–243 K) as demonstrated in [3], chapters 2 and 3. Mostly, ozonolysis of olefins, except in solid phase, is carried out in various solvents such as paraffins, halogenated hydrocarbons, oxygen, sulfur, and nitrogen containing hydrocarbons like ahcohols, glycols, aldehydes, ketones, acids, ethers, esters, amines, amides, nitriles, sulfoxides, mineral acids, bases, and their mixtures, *etc*. In most cases the reaction products are not separated from the reaction mixture except for the purposes of ozonide obtaining, and the oxidates are subject to hydrolysis, reduction, or oxidation [1, 3].

The hydrolysis is applied for preparation of aldehydes [70] and ketones [71]. The reductive decomposition is carried out in the presence of Zn/AcOH, SO_3^{-2}, HSO_3^{-1}, $LiAlH_4$, $SnCl_2$, ArP_3, Ph_3P, SO_2, $(CH_3)_2S$, H_2/catalyst. The reduction by metal hydrides leads to alcohol formation in the decomposition products mixture while the use of other reductors yields carbonyl compounds. Actually there are no clear requirements to the selection of the most appropriate reductor, but it turned out that dimethylsulfoxide is probably [72] the most preferable reductor in methanol solution. The ozonolysis in the presence of tetracyanoethylene yields directly carbonyl moieties omitting the reduction step [73]. A novel modification of the conventional methods of ozonolysis is exemplified by the ozonolysis of silica gel adsorbed alkenes (acetylenes) [74] and selective ozonolysis of polyalkenes, controlled with the help of dyes introduced in the reaction mixture [73]. Some examples of ozonolysis

Table 6

Preparation of aldehydes, ketones and alcohols during alkenes ozonolysis with consecutive reduction

No.	Substrate	Conditions	Product	Yield, %
1.		1. EtOAc, 253- 243 K 2. Pd/$CaCO_3$/H_2		61
2.		1. n-C_6H_{14} 2. Zn/HOAc		59
3.		1. MeOH/233 K 2. Na_2SO_3/H_2O		65
4.	$Me(CH_2)_5CH=CH_2$	1. MeOH/243÷ 213 K 2. Me_2S	$Me(CH_2)_5CHO$	75
5.	n-Bu-OOCCH=CHCOO-Bu-n	1. MeOH/208÷ 203 K 2. $(MeO)_3P$	n-Bu-OOCCHO	78
6.		1. MeOH/238÷198 K 2. NaI/MeOH/HOAc		75
7.		EtOAc/$(CN)_2C=C(CN)_2$,203 K	$MeCO(CH_2)_3COMe$ + 	61
8.	$Me(CH_2)_5CH=CH_2$	1. n-Pentane/235 – 231 K 2. $LiAlH_4$/Et_2O	$Me(CH_2)_5CH_2OH$	93
9.	$H_2C=CH(CH_2)_8COOH$	1. MeOH/273 K 2. $NaBH_4$/NaOH/ EtOH/H_2O	$HOCH_2(CH_2)_8COOH$	91

using various reductors for ozonides decomposition are given in Table 6 [75-80].

Ozonolysis is a powerful chemical method for economical and ecologically pure preparation of various carbonyl compounds [81].

The ozonolysis of cyclic alkenes in protic solvents followed by reductive decomposition of the formed hydroperoxides is a classical method for dialdehydes synthesis [82]. This method is applied for the preparation of 3-ethoxycarbonylglutaric dialdehyde by ozonolysis of ethyl 3-cyclopentenecarboxylate. The dialdehyde is an intermediate in the synthesis of dolazetrone mesitilate, which is an active medical substance in ANZEMET anti-emetic. Zn/AcOH, phosphines, amines, and sulfides such as 3, 3'-thiodipropionic acid and its salts are the most suitable reductors for this system. Their efficiency is comparable to that of methyl sulphide but without its shortcomings. The polymer immobilized 3,3'-thiodipropionic acid is also very active in this reduction reaction [82].

The efficient conversion of oximes into the corresponding carbonyl compounds can be also carried out through ozone oxidation [83].

The application of ozone is a new and convenient way for the preparation of cyanoacetylaldehyde (3-oxopropylonitrile) (1) and its stable dimethyl acetal (3,3-dimethoxypropylonitrile) (2) used as valuable intermediates for organic synthesis [84]. For this purpose the ozonolysis of (E)-1,4-dicyano-2-butene or 3-butylonitrile is carried out. Then the oxidates are treated by DMS yielding (1). Further, compound (1) can be used either directly in the next reactions or is transformed into (2). The (2) output amounts are from 67 to 71 %. The acetal can be again hydrolyzed to (1) by treatment with ion-exchange resin Amberlyst-15 [84].

The easily available allylphenyl ethers are ozonized at 233 K, treated with DMS giving solutions of the corresponding phenoxyacetaldehydes which are purified by column chromatography. Their reaction with 1-methyl-1-phenylhydrazine yields the corresponding hydrazones [85].

Quinolinealdehyde derivatives can be synthesized by ozonolysis of the respective quinolineolefins at 213-201 K in methanol or ethanol solution with consecutive reduction of DMS at the same temperatures. Then the reaction mixture is heated to room temperature for 1 h. The yield of the products amounts to 29 %. [86].

6-Chloro-2-hexanone is prepared from 1-methylcyclopentane via three-step scheme: a) ozonolysis of 1-methylcyclopentane in carboyilic acid solution to 1-methylcyclopentanol; b) conversion of 1-methylcyclopentanol into 1-methylcyclopentyl hypochloride using NaClO; c) cyclization of 1-methylcyclopentyl hypochloride in 6-chloro-2-hexanone [87].

Ozonation is a stage in the synthesis of optically pure (R)-(+)-4-methyl-2 cyclohexen-1-one from (R)-(+)-pulegone and hydroxy ketone from (-)-*cis*-pulegol [88].

Polycarbonyl compounds and aldehyde-acids are the ozonolysis products of (+)-4a-[1-(triethylsiloxy)-ethenyl]-2-carene [89].

Carbonyl oxides obtained from vinyl ethers ozonolysis undergo rapid [3+2] cycloaddition with imines giving the corresponding 1,2,4-dioxazolidines in yields of 14–97 % [90].

Carbonyl oxides can be also used for the synthesis of 3-vinyl-1,2,4-trioxalanes (*a*-vinylozonides) by a [3+2] cycloaddition with *a*-, *b*-unsaturated aldehydes. However, *a*-, *b*-unsaturated ketones are practically inactive in this reaction. The reaction of 3-vinyl-1,2,4-trioxalanes with ozone leads to the formation of the corresponding dizonides [91].

The carbonyl oxides prepared from the ozonolysis of enol ethers (*e.g.*, 1-metoxy-4,8-dimethylnone-1,7 diene) undergo stereoselective intramolecular cycloaddition with inactivated alkenes yielding bicyclic dioxalanes. The latter are easily converted into *b*-hydroxycarbonyl species and 1,3-diols by catalytic hydrogenation thus providing a new approach to the synthesis of 1,3-oxygenated products [92].

The ozonolysis of vinyl ethers is discussed in detail in [93].

The synthesis of 1,2-dioxalanes is carried out by ozonolysis of 1,1-disubstituted nonactivated olefins. Thus the ozonolysis of cyclopropyl-1,1-disubsituted olefins does not produce carbonyl oxides, but formaldehyde oxide. The latter can react with the initial olefin leading to the formation of 2-dioxalanes with 10 % yield. At the addition of "foreign" olefins or aldehydes other dioxalanes and normal ozonides can be obtained [94].

The cycloalkenes ozonolysis in the presence of methyl pyruvate results in tri-substituted ozonides formation. The latter contain three reaction centers (peroxides, proton on the ozonides cycle and methoxy-carbonyl group) accessible for various functionalization. The cyclohexene ozonolysis in the presence of methylpyrovate gives ozonide whose treatment with PPh_3 or Et_3N yields $CHO(CH_3)_4CHO$ and $CHO(CH_3)_4COOMe$ (after esterification), respectively. This method proved to be a very convenient and practical way for the synthesis of linear compounds containing various terminal groups from symmetrical cycloalkenes, in two steps and with good yields [95].

The direct conversion of olefins into esters is accomplished during mono-, di- and thi-substituted olefins ozonolysis in 2.5M methanol sodium hydroxide-dichloromethane solution. The methyl esters are obtained in high yields. Thus, 3-benzyloxy-1-nonene (5b) is transformed into 78 % yield 2-benzyloxyoctanoate (7b) in [96].

The ozonolysis of acyclic alkenes including terpenes is reviewed in [97].

The role of ozonolysis as ecological process for the selective and specialized oxidation of petrochemical olefins and cyclic alkenes, for the manufacture of biologically active substances and normal organic compounds is thoroughly discussed in [98].

In [99] the data on ozonolysis of acyclic and cyclic mono-, di- and trienes in the various stages of the synthesis of insect pheromones and juvenoids are summarized.

N-acylated esters of (cyclohexa-1,4-dienyl)-*L*-alanine are ozonized aiming at the synthesis of novel unnatural amino acids. The combined reduction and ozonolysis followed by condensation with a suitable nucleophile results in transformation of the aromatic ring of *L*-Phe to isooxasolyl, *N*-phenylpyrazolyl and to bicyclic pyrazolo[1,5-a]pyrimidine groups. The preparation of heterocyclic alanine derivatives is reported [100].

Thymidine diphospho-6-deoxy-a-*D*-ribo-3-hexulose synthesized by *D*-glucose ozonolysis of methyl-glucophosphate is used as a central intermediate in the biosynthesis of di- and tridioxy sugars [101].

The ozonolysis of vinyl halides followed by reductive regio- and stereo-controlled intramolecular cyclocondensation is a key stage in the synthesis of amino sugars [102].

The ozonolysis of pyrols, oxazoles, imidazoles, and isooxazoles demonstrates another application of this reaction to the organic synthesis. Pyrols are efficient protective groups of the amino functions in the synthesis of *a*-aminoalcohols, *a*-aminoketones, *a*-aminoaldehydes and some peptides. The oxazole ring is also known as a protective group in the peptide synthesis [103].

The 1-substituted imidazoles ozonolysis leads to the formation of the corresponding *N*-acylamides, which are important amine or acyl derivatives [104].

Some novel tetraacetal oxa-cages and complex tetraquinone oxa-cages are synthesized from alkylfuranes by a three-stage reaction. Oxo rings in the tetraacetals are obtained by the ozonolysis of *cis*-endo-1,4-diones (norbornene derivatives) in dichloromethane solution at 195 K and consecutive reduction with DMS. The tetraquinone oxa-cages are obtained in the cis-endo-1,4-diones ozonolysis in dichloromethane solution at 195 K and TEA treatment [105].

A method for cleavage and oxidation of C_{8-30} olefins to compounds containing terminal carboxylic acid groups is reported in [106]. The process is promoted by oxidation catalysts, such as Cr, Mn, Fe, Co, *etc*.

The conversion of ethane to methanol and ethanol by ozone sensitized partial oxidation at near atmospheric pressure has been quantitatively studied. The effect of temperature, oxygen concentration in the inlet gas, contact time in the reactor, and ozone concentration in oxygen has been evaluated. The selectivity in regard to ethanol, methanol, as well as the combined selectivity towards formaldehyde-acetaldehyde-methanol-ethanol is also discussed [107].

Upon studying the ozone-induced oxidative conversion of methane to methanol and ethane to ethanol it has been established that these reactions do not occur in the absence of ozone which clearly suggests that the partial oxidation is initiated by the oxygen atoms generated from the ozone decomposition [87, 108].

Ortho-selective nitration of acetanilides with nitrogen dioxide in the presence of ozone, at low temperatures results in ortho-nitro derivatives formation in high yields [109].

The ozone mediated reaction of nonactive arenes with nitrogen oxides in the presence of suitable catalysts is reported as a new method for the synthesis of the corresponding nitro derivatives with high yields [110].

The ozone induced reaction of polychloro benzenes and some related halogeno compounds with nitrogen dioxide is a novel non-acid methodology for the selective mono nitration of moderately deactivated aromatic systems [111]. In the presence of ozone and preferably with methanesulfonic acid as a catalyst, the polychloro benzenes undergo mononitration with nitrogen dioxide at low temperatures giving polychloronitrobenzenes in nearly quantitative yields [111].

The ozone mediated reaction of aromatic acetals and acylal with nitrogen dioxide is suggested as a novel methodology for the nuclear nitration of acid sensitive aromatic compounds under neutral conditions [112].

Mineral and acid-free nitro compounds are prepared from CH_2Cl_2 soluted pyridine or its derivatives treated with $NO_2/O_2/O_3$-mixture for 8 h [113].

The nitration of aromatic compounds with nitrogen oxides in the presence of ozone is a catalytic process [114].

The stereoselective synthesis of vinyl ethers is accomplished by *N*–(arylidene (or alkylidene) amino)–2-azetidinones reaction with ozone and $NaBH_4$ treatment resulting in di- and trisubstituted olefins derivatives [90].

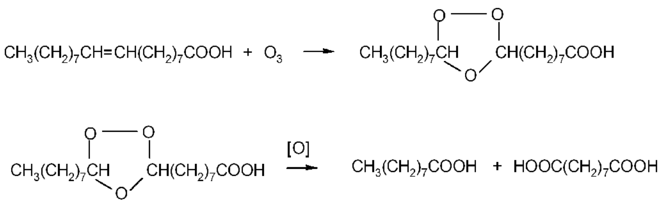
The steroeselective synthesis of (2s, 3s) norstatine derivatives is carried out through aldehydes ozonolysis in the presence of lithium methoxyallene [94].

An interesting method of succinic acid preparation from butadiene rubber ozonolysis is suggested [115].

The preparation of *a*-phenyl ketone, *w*-carboxylate-ended telehelic methyl methacrylate oligomers by the ozonolysis of regioregular methyl methacrylate-phenylacetylene copolymers is described in [116]. The oligomers have molecular mass varying from 1600 to 4500 (with respect to the initial copolymers) and polydespersity less than 2.

Ozone is also a very convenient agent in the manufacture of organic ceramics [117].

The ability of ozone to destroy the double C=C bonds in organic compounds is the reason for its wide application in the preparation of bifunctional compounds. This is the principle that lies in the organization of the manufacture of dodecanedicarboxylic acid (1) and azelaic acid (2). The initial substrate for the preparation of (1) is cyclododecane, which is obtained from the trimerization of butadiene and partial hydrogenation and (2) is prepared on the base of oleic acid:



The main part of dicarboxylic acids is used in the manufacture of polyester fibers, and the azelaic acid esters (*n*-hexyl, cyclohexyl-, *iso*-octyl- and 2-ethylhexyl ester) are excellent plastisizers and synthetic lubricants.

The action of ozone is also used in pharmaceuticals in the preparation of valuable hormone products. Thus the C=C bond at C_{17} in the side chain of stigmasterol is destroyed by ozone yielding progesterone – an initial source for many hormones such as cortisone, male and female sex hormones, *etc*.

The method of selective decolorization of fabrics containing cellulose materials, such as cotton and oxidizing dyes [118], includes the following steps: application of oxidation blocking agent to the fibers; contact of the fibers with the oxidizing reagent in gas or evaporated state in the presence of moisture till the oxidation and decolorization of the dyer is carried out; interruption of this contact before the beginning of a substantial destruction of the fiber. The oxidizing agents are selected among ozone, chlorine and nitrogen oxides and sulfur dioxide flow. The application of ozone for decolorizing indigo-painted cotton jeans after this procedures results in jeans material which does not turn yellow for 6 months while the untreated goes yellow much more rapidly [118].

The changes in the composition and chemistry of UV/ozone modified wool fiber surfaces [119] are investigated by means of photoelectronic spectroscopy (XPS). The oxidation of the disulfide sulfur to sulfone groups ($^{-}SO_3H$) containing S^{6+} approaches almost 90 % conversion. This is much more than the conversion levels by using oxygen plasma. Ozonolysis results in rise of C–O groups content, particularly of the carbonyl ones [119].

The process for producing cellulose fibers and moldings such as fibers, filaments, threads (yarn), films, membranes in the form of flat, pipe and empty fibrous membranes, etc. is carried out using ozone [120]. They are produced by extrusion of cellulose solutions in tertiary amine aminooxides and in some cases in water (particularly *N*-methylformaline *N*-oxide and water); regenerating bath and water for washing by treatment with hydrogen peroxide, peracetic acid and ozone or chlorine dioxide for the regeneration of tertiary amines oxides. The introduced compounds can be enzymatically or catalytically destroyed before solvent and water regeneration.

Pitch-based carbon or graphite fibers of high tensile strength are manufactured by primary treatment of the pitch-based fibers with high concentrated ozone for a short period; then the treatment by ozone-free gases follows; in the next step they are subject to carbonization of graphitization to give elliptical fibers of long wool similar structure. Upon treatment in the absence of ozone the fibers stitched during graphitization [121].

The EPR analysis of thermal decomposition of peroxides in ozonized polypropylene fiber for grafting shows that the decomposition of the peroxide groups begins at about 343 K. The generation of several peroxides radicals is registered; the access of the fiber to the spin sample is enhanced through oxidation. Small amounts of RO_2 radicals with lifetime of a couple of weeks have been identified. The integral intensity of the EPR-signal rises with time and ozonation temperature [122].

Ozonolysis modifies the diffusion pattern of liquid monomers in polypropylene matrix as their addition occurs in the amorphous phase. The appearance of intra-morphological structure and peroxides localization upon ozonolysis of polypropylene (granules and fibers) is monitored using electron spin resonance and transmission electron microscopy [123].

Upon ozonolysis, UV-radiation and plasma treatment polymer peroxides are generated on the surface of films from polypropylene, polyurethanes and polyester fibers [124]. Their thermal and reductive-oxidative decomposition have been studied by means of functional analysis using peroxidase and iodide. However, their disposition in the polymer specimen is quite various thus impeding their analysis and depends on the treatment agent. For example, the treatment with plasma generates easily accessible peroxides in polyurethane films while the UV-radiation and ozonation leads to formation of peroxides incapable of reacting with aqueous solution of peroxidase. The redox decomposition of the peroxide groups by ferro-ions at 298 K has shown that less than 50 % of the peroxides may react with ferro-ions at rate constants similar to those of hydrogen peroxide in aqueous solution. The thermal degradation of peroxides does not follow first order kinetics, most probably because of the generation of various peroxide species, characterized by different rates of decomposition. The lowest rate constant of decomposition is observed at 335 K is 3.10^{-3} min^{-1}, which does not depend on the polymer nature and the method of peroxides generation [124].

Ozone-induced graft polymerization onto polymer surface is an important and convenient method for polymer modification [125].

Ozone-induced graft copolymerization of polyethylene glycol monomethyl ether methacrylate onto poly(etherurethane) improves the hydrophility and water absorption. The autoaccelerated effect in ozone-induced polymerization has been also discussed [126].

The modification of the surface properties of polypropylene and block copolymer is carried out by ozone treatment. Thus, the wet ability of the polymers is improved – the contact angle of water becomes ≤ 67^0. The break of the polymer chain and carboxyl groups formation are accelerated by using high ozone concentrations. The cut-off fragments resulting from the ozone treatment are removed from the surface by ultrasound and organic solvents [127].

The low temperature nonelectrolytic nickel plating onto three types of polypropylene is carried out by substrate pretreatment with ozone. The latter modifies the polymer surface for galvanization while the combination of polar with anchor effect as a result of the ozone etching enhances the adhesive properties of the polymer surface. The washing of the material after ozonolysis is obligatory to ensuring proper adhesion of the material [128].

The surface properties of polypropylene (I), 100 μm films from (I), ethylene-propylene block polymer (II), or ethylene-propylene polymer prepared by the random method (III) can be improved by ozonation at concentrations of 1.38, 0.64, and 0.41 mol %, respectively. The adhesion of dyes, coloring agents, dye layers, on (I) is substantially improved and depends on the substrates in the following order: (II) > (III) > (I). It has been found that for each sample there are optimum conditions of ozonation. Reactive dyes such as epoxy and acrylo urethane resins impart a better adhesion force than the conventional nonreactive acrylic or vinylchloride resin [129].

Freshly extruded, 50 μm C_2H_4-ethyl acrylate-maleic anhydride copolymer film is treated by 500 ml/m^2 oxygen containing 10 g/m^2 ozone and is calendered with 200 μm monolayer C_2ClF_3 – polymer film at 288 K to produce moisture-proof packaging material with intra-layer adhesion of 800 g/15 mm and thermosealing force of 3.6 kg/15 mm against 250 and 1.3, respectively in the absence of ozone treatment [130].

Methylmethacrylate polymers with good thermal degradation resistance are prepared by ozonolysis [131] whereby the end unsaturated groups are converted into carbonyl or carboxyl ones. Ozone/air mixture is blown through a 10 g Acrypet VH solution in CH_2Cl_2 at 195 K followed by exposure only to air for 60 min and after solvent removal the solid residue is dried in vacuum at 570 K for 8 h. The polymer thus obtained is characterized by an initial temperature of thermal degradation of 588 K against 570 K for the polymer without ozone treatment [131].

The surfaces of propene polymer moldings are treated with ozone to improve their hydrophility. The ozone treatment of the surfaces for 8 h reduces the contact angle of water from 100 to 81^0 [132].

Ozonation of PVC latex is also carried out for removal of vinyl chloride residues. The aqueous dispersions of saturated polymers are treated with ozone and the vinyl monomers are removed [133].

Graft polymerization of vinyl monomers onto Nylon 6 fiber is carried out after ozone oxidation of the fibers or films from Nylon 6 with vinyl monomers such as acrylamide, methylmethacrylate and vinyl acetate. The molecular mass of Nylon 6 decreases slightly upon ozonation. For acrylamide graft polymerization system the preliminary treatment in air or vacuum by γ-rays radiation prior ozonation results in higher graft percentage. For methyl methacrylate the apparent graft percentage does not rise with the ozonation time. However the apparent graft percentage for vinyl acetate is increased with the ozone time treatment [134].

The adhesion of PVC-, fluropolymer or polyester-coated steel panels is improved by treatment with 5–50 % solution of H_2O_2 or ozone [135].

Synthesis of water-soluble telehelic methyl-ketone-ended oligo- *N,N*-dimethylacrylamides by the ozonolysis of poly(*N,N*-dimethylacrylamide-stat-2,3-dimethylbutadiene) is reported in [136].

The synthesis of telehelic methylmethacrylate and styrene oligomers with fruorophenyl ketone end groups is accomplished by the ozonolysis of copolymers containing 4-flurophenyl butadiene units [137].

Graft polymerization of acrylic acid is carried out into preliminary ozonized siloxane matrixes [138].

The manufacture of base discs for laser recording material is realized by covering of the plastic substrates surface with solid polymer layer possessing directing channels and/or signal holes. The surface of the plastic substrate is preliminary cleaned by UV/ozone exposure before the formation of the hardened polymer layer [139].

The controlled degradation of polymers containing ozonides in the main chain takes place in the presence of: 1) periodate suported on Amberlyst A26 (SPIR); 2) diphenylphosphine deposited on polystyrene (SPR); 3) boron hydride supported on Amberlyst A26 (BER) [129]. Poly(butyl)methacrylate-copolymers are prepared by emulsion polymerization. These materials and the homopolymer poly(butyl)methacrylate are ozonized at various temperatures and treated by any of the reagents described above, thus giving telechelic oligomers in 99 % yield. Molecular mass varies when the ozonation temperature is changed. The end aldehyde groups are registered using ^{1}H and ^{13}C -NMR spectroscopy; the end hydroxyl groups are observed by means of FT-IR and ^{13}C-NMR; the presence of hydroxyl groups is confirmed by tosylate formation; the carboxyl groups are identified by FT-IR and ^{13}C-NMR and quantitatively determined by titration; in the SPR-generated oligomers the content of aldehyde groups constitutes about 80 % of the end functional groups. The oligomers obtained in BER and SPIR contain 99 % hydroxyl and carboxyl groups [140].

Polyethylene fibers are subject to ozone treatment to modify their surface [141]. The analysis of the surface is carried out by means of X-ray photoelectron (ESCA) and IR (FT-IR) spectroscopy. Carbon (C) and oxygen (O) were the main atoms monitored with ESCA (C-1s, O-1s areas) on the treated fibers. The analysis of C-1s peaks (C_1, C_2 and C_3) reveals that the oxidation level depends on the ozonation time. The components of 1s peak (O_o, O_1, O_2) are very useful for carrying out the surface analysis. They demonstrate the presence of carbonyl groups (1740–1700 cm^{-1}) even on the untreated fibers whose intensity rises with treatment time. Ozonolysis is directed from the surface to the fiber bulk. This is confirmed by the great enhancement of the carbonyl bond band after 3 h ozonation. The thermal analysis suggests structural and morphological changes of the fiber when ozonation time exceeds 2 h [141].

The processing of fiber-reinforced plastics is performed by blowing an ozone-oxygen mixture (flow rate of 0.4 l/min) for 5 h through a CH_2CL_2 solution containing glass reinforced fiber particles (1mm diameter) filled with $CaCO_3$ and unsaturated polyester. The fibers emerge on the surface till a fine powder is precipitated [142].

The manufacture of laminates through heat-sealing method involves the application of electric crown, UV-radiation or ozone exposure [143].

The manufacture of pour point depressants for oils, particularly useful for diesel oils, is carried out by oxidative degradation of waste polyethylene and/or polypropylene (I) with ozone at 303–423 K. 1000 g Waste (I) is exposed to ozone action at 423 K for 5 h giving the pour point depressant. The addition of 1 % depressant to diesel oil reduces the solidification of the oil from 253 to 238 K and the temperature of filter plugging from 264 to 253 K [144].

3.2. Inorganic Productions

Stainless steel parts are treated by ozone for surface passivation. The parts are heated in oxidative or inert atmosphere at a temperature of condensation lower or equal to 263 K. The unreacted ozone is re-used [145].

The main passivating agent is oxygen in combination at least with ozone. The system is particularly appropriate for passivation of metals (*e.g.*, stainless steel, Ti, *etc*.) equipment, used in chemical plants and exposed to strong corrosion action at high temperatures and pressures [146].

To increase the corrosion resistance of metals and alloys they were exposed from 1 s to 10 min in cold plasma under pressure 1–103 Pa and 100–5000 V in atmosphere containing O_2, O_3, N_2, H_2, air, CO_2, CO, N-oxides, H_2O (gas), combustible gas and/or inert gas. Thus, 17 % of C0-ferrite stainless steel is subject to plasma treatment for 4 min at 103 Pa, 100 mA, and 250 V in nitrogen-oxygen mixture with 20 % oxygen. The corrosion resistance was evaluated by treatment of the sample with a solution containing 17 ml 28 % $FeCl_3$, 2.5 ml HCl, 188.5 ml H_2O, and 5 g NaCl. The sample shows relatively good resistance as compared with the untreated one [147].

Electrochemical tests reveal the influence of dissolved ozone on the corrosion behavior of Cu-30 Ni and 304L stainless steel in 0.5N sodium chloride solutions [148]. These experiments include: measurements of the corrosion potential as a function of the time and ozone concentration; cyclic polarization experiments; isopotential measurements of the current density and study of the film components. The results of these experiments show that for Cu-30 Ni and 304L stainless steel the corrosion potential is shifted to the more noble values (300 mV) at $[O_3] < 0.2$–0.3 mg/l. At higher concentrations it remains unchanged. The dissolved ozone reduces the corrosion level for Cu-30 Ni alloys, which is evaluated by the substantial decrease in the current density at constant applied potential. The improvement of the corrosion resistance should be related to the decrease of the thickness of the corrosion products film and to the higher oxygen fraction as compared with the chloride in the same film. For stainless steel the differences in the passivating films in ozonized and nonozonised solutions are negligible as it is shown by spectroscopy [148].

Laboratory experiments have been carried out to study the ozone application for acid oxidizing leaching of chalcopyrite with 0.5 M H_2SO_4. For evaluating of the reaction mechanism the effect of particles size distribution, stirring and acid concentration, the dissolution reaction and reaction kinetics on the leaching have been investigated. The reaction rate is governed by ozone diffusion to the reaction mixture. Ozone is an efficient oxidizer and the process is most effective at 293 K [149].

The rate of acid leaching of chalcopyrite depends on the use of ozone as an oxidizing agent in sulfuric acid solutions. The leaching of chalcolyrite follows a parabolic law [150]. The use of ozone as an oxidizer provides conditions for the formation of elemental sulfur on the leached surfaces. The rate of leaching is reduced with temperature as the ozone solubility decreases with temperature. The results show that ozone is the best oxidizing agent for acid oxidizing leaching of chalcopyrite and may be applied in pilot plants for regular manufacture.

We have studied the possibility of using ozone for improvement of Ag extraction from polymers deposits in a flotation plant in the town of Rudozem (Bulgaria). It has been found that upon bubbling of ozone (1 vol % concentration, flow rate – 300 l/h) through flotation machine the degree of Ag extraction is increased by 1–2 % [150].

The redox leaching of precious metals from manganese-containing ores carried out by other authors show also positive results [151].

Molybdenite flotation from copper/molybdenum concentrates by ozone conditioning results in relatively pure copper-free molybdenum. The process including multi-step ozone flotation proves to be a technical and economical profitable method [152].

The manufacture of potassium permanganate is accomplished by melting of Mn-containing compounds with KOH, dissolution of the melt and the solution oxidation. To reduce the energy consumption $Mn(NO_3)_2$ is used as a Mn-containing compound. It can be easily alloyed with KOH in a 1:5–1:10 ratio at 523–573 K. Then the product is dissolved in 20–25 % KOH solution, the solid residues is removed, saluted in 3–5 % KOH and the solution is oxidized by ozone-air mixture [153].

In the manufacture of silicon carbide ceramics melted organosilicon polymer is oxidized with 0.001 vol % ozone. Polycarboxylstyrene is the preferred polymer. The ceramics obtained is characterized by high thermal resistance and acceptable physical properties [117].

Mixtures containing In- and Sn-compounds are molded and sintered in a furnace in air atmosphere containing ≥ 1000 ppm ozone. The ITO ceramics thus obtained are characterized by high density at low temperature sintering for a short time [154, 155].

A method for oxidizing carbonaceous material and especially for bleaching gray kaolin for subsequent use as coating or filler for paper in the presence of ozone is reported in [156].

The manufacture of mercury (I) chloride includes the reaction of Hg with hydrochloric acid in the presence of water and subsequent removal and drying at 368–378 K. Ozone (0.1 g/g product) is bubbled through the reacting mass to increase the product yield and quality [157].

Arsenic acid is prepared from $(As_2Cl_6)^{2-}$ -ions by ozonolysis [158].

The removal of color and organic matter in industrial phosphoric acid by ozone and the influence on activated carbon treatment is described in [148]. Industrial phosphonic acid containing 42–45 % P_2O_5 and 220–300 mg/l organic matter (OM) is subject to combined treatment with ozone and activated carbon. The independent ozonation results in removal of the initial dark color of the acid and the organic matter. It is only through absorption on activated carbon that the level of OM could be reduced to 80 % per 25 g/kg P_2O_5. The ozonation prior to adsorption enhances the efficiency of the activated carbon effect and decreases its specific consumption [159].

The fabrication of high-Tc superconductors is carried out using ozone-assisted molecular beam epitaxy (MBE). It includes the simultaneous evaporation of the elementary components and application of ozone as a reactive oxygen source. The ozone priority over the other oxygen forms is that it is rather stable and could be produced and supplied to the substrate in a very pure state using simplified apparatus ensuring a well defined flow of oxidizing gas. In order to prepare films with high temperatures of superconductivity the growth should be carried out at relatively low stresses in the system. In addition, the surface during film growth can be analyzed by reflectance high energy electron diffraction. The most recent improvements in ozone-assisted MBE for family of $YBa_2Cu_3O_7$- delta films are described. The results show that this technique is very appropriate for growth of high quality superconductive films and could be ideal for the manufacture of such structures [160].

The growth of superconductive oxides under vacuum conditions compatible with MBE requires the use of activated oxygen. The atomic oxygen or ozone appears to be such species [150]. The characteristics of a radio-frequency plasma source for molecular beam epitaxial growth of high-Tc superconductor films (200 E) from $DyBa_2Co_3O_7$ on $SrTiO_3$ are described and discussed in [161].

An apparatus for the preparation of pure ozone vapor to be used for ***in-situ*** growth of superconducting oxide thin films are designed [151]. Pure condensed ozone is produced from distillation of diluted ozone-oxygen mixture at 77 K. The condensed ozone is heated until the pressure of its vapors approaches the necessary for an adequate flow of ozone gas to the chamber of thin films growth. The thin films from $YBa_2Cu_3O_7$ with zero resistance at temperatures of about 85K grow at ozone pressure in the chamber of $2 \cdot 10^{-3}$ Torr even without subsequent untempering. It should be noted that in contrast to other highly reactive oxygen species ozone can be prepared and stored in a very pure form, which makes it very convenient for studies on the kinetics of growth and oxidation of films with a well defined gas [162].

A patent for preparation of oxides superconductors M-M^1-M^2-M^3 includes ozone oxidation where: M = elements of III B groups such as: Y, Sc, La, Yb, Er, Ho or Dy; M^1 = elements from II A group, such as: B, Sr, Ba or Ca; M^2 – Cu and one or more elements from I B group such as Ag or Au; M^3 = O and one or more elements belonging to VI A group like S or Se and/or elements from VII A group as F, Cl or Br. The superconductors thus prepared have high critical temperature and high critical current densities [163].

The manufacture of bismuth-, copper- alkaline earth oxide high-temperature superconductors is carried out through calcination and/or sintering in ozone-containing atmosphere with $Bi(OH)_2$, $Ca(NO_3)_2$ and $Sr(NO_3)_2$ and subsequent treatment by $CuCO_3(OH)_2$; the components are dried, calcinated in ozone containing air, molded and dried in air atmosphere. Their temperature of superconductivity is 107K and the critical current density is 405 A/cm^2 [164].

A low temperature method for preparation of superconductive ceramic oxides is described in [165]. It includes the treatment of the substrate heated surface by ozone to the complete evaporation of the other components thus forming a superconductive ceramic oxide.

The manufacture of rare earth barium copper oxide high-temperature superconductor ceramics is carried out by sintering at 1203–1273 K in ozone atmosphere containing oxygen. Y_2O_3, $BaCO_3$ and CuO are mixed, calcinated, pulverized, pressed, and sintered at 1223 K in the presence of ozone-oxygen mixture after which they are gradually cooled to the critical superconductive temperature 94 K [166].

A review devoted to the growth of co-evaporated superconducting yttrium barium copper oxide (YBa_2CuO_7) thin films oxidized by pure ozone is presented in [167].

The removal of organic pollutants from the surface of supports for microelectronics purposes is conducted by UV/ozone treatment [168].

Low temperature silicon surface cleaning is carried out by fluoric acid (HF) etching, washing, cleaning with deionized water, N-gas blowing, /UV-ozone treatment. This is a treatment preceding the process of silicon epitaxy [169-171].

The method for total room temperature wet cleaning of silicon surface implies the use of HF, H_2O_2, and ozonized water and is 5 % more economical than the standard procedure of wet cleaning [172].

The removal of resist films supported on semiconductive substances is accomplished by using ozone [173].

The application of ozone for reducing the temperature and energy in the process of very large scale integration (VLSI) is described in [174, 175]. The main problems under discussion are as follows: 1) cleaning of Si-support with ozone by two methods: dry process combined with UV and the wet one – with ozonized water; 2) stimulation of Si thermal oxidation with ozone; 3) deposition of SiO_2 under atmospheric pressure and low temperature *via* chemicals evaporation using tetraethylorthosilicate and ozone; 4) deposition of Ta_2O_3 at atmospheric pressure and low temperature applying $TaCl_5$ and ozone; 5) tempering with ozone and UV-radiation of Ta_2O_5 films used for dielectric for memory units, this treatment reduces the current permeability into the film; 6) etching of photoresistant materials by $O_2/O_3/CF_4$ and 7) the effect of ozonator charge and injection of CF_4 [174, 175].

The cleaning of synchrotonic radiation optics with photogenerated reactants has a number of priorities over the methods of discharge cleaning [176]. Upon discharge cleaning, the discharge particles should react with the surface contaminants until its sheilding by the rough discharge elements which may pollute or destroy the surface. Contrary, if the particles can be photon generated near the surface, the problem with the protection drops off and in some cases the cleaning can be more efficient. An estimation of the various methods for cleaning was made comparing the rates of polymethylmethacrylate films removal. A number of various light and geometry sources have been tested. The highest rate of cleaning was achieved upon using UV/O_3 cleaning method at atmospheric pressure. This method has been widely applied for cleaning semiconductive surfaces from hydrocarbon contaminants. It is noted that it is also effective in removing graphite-like pollutants from synchrotonic radiation optics. It proves to be more simple, economical, and selective method as compared with other cleaning method. Although it requires the drilling of a hole in the vacuum chamber, the cleaning of the optics can be carried out without disassembling, which saves much time. This method is successfully applied for cleaning grates and reflectors in several beams [176].

Native oxide growth and organic impurity removal on silicon surface is carried out by ozone-injected ultrapure water [166]. In order to manufacture high-efficient and reliable ULSI-units the further integration and minimization is in progress. The cleaning with $H_2SO_4/H_2O_2/H_2O$ is accompanied by serious problems: a great amount of chemical wastes which must be suitably treated is obtained. The cleaning technology with ultrapure water includes ozone injection in concentrations of 1–2 ppm. This method is very efficient in removing the organic impurities from the surface for a short time and at room temperature. The process wastes can be treated and recycled. The ozonized water components can be easily controlled [177].

The reaction mechanism of chemical vapor deposition using tetraethylorthosilicate and ozone at atmospheric pressure is reported and discussed in [178].

Covering of semiconductor devices with silica films is carried out via CVD using $Si(OEt)_4$ and ozone. The deposition process is followed by heating in oxygen atmosphere with simultaneous UV radiation. The SiO_2-film thus formed can improve the water resistance of semiconductive devices [179].

The fabrication of nondoped silicate glass film with flat structure by O_3-TEOS deposition includes three stages: 1) substrate treatment; 2) formation of Al conducting layer on it using oxygen plasma through heating and 3) formation of SiO_2-film on the substrate by plasma using ozone and TEOS [180].

In [170] the future trends for interlayer dielectric films production and their formation technologies in ULSI multilevel interconnections are reviewed. The properties of the interlayer dielectric films and their preparation technologies should satisfy the following three requirements: 1) available for disposition (setting) on large surface; 2) low dielectric constant and 3) low deposition temperature. Two techniques have been developed for the selective deposition of SiO_2-films, which is the best way for achieving a complete planirization of the interlayer surface of dielectric films: low temperature liquid phase deposition using a saturated aqueous solution of hydrofruorosilicon acid H_2SiF_6; half-selective SiO_2-films deposition at 663 K with $Si(OC_2H_5)_3$ and ozone and preliminary treatment with tetraflurocarbonic (CF_4) plasma on TiW or TiN surfaces [181].

Lead zirconate and titanate thin films are successfully prepared by reactive evaporation. The elements Pb, Zr, and Ti are evaporated in ozone-oxygen mixture. The films obtained have equal thickness and composition per large surface (in the range of ±2 % from the 4-inch support) [182].

Ceramic coatings on substrates are formed in the presence of ozone [183]; the substrates (silicon checks) are covered (dipped) in a solution of one or more (partially) hydrolyzed pre-ceramic silicon alholates with general forrmula $R_xSi(OR)_{4-x}$ (R = C_{1-20} alkyl, aryl, alkenyl or alkinyl; x = 0-2). Further, the solvent is evaporated to form a coating which is subsequently heated in the presence of ozone up to 313–373 K thus converting into a ceramic coating. It in its turn may be covered also by a protective layer containing Si, or Si and C, or Si and N, or Si, C and N, or SO_2 and oxide. These coatings which are abrasive-, corrosive- and thermo-resistant have also a small number of defects and suppress the diffusion of ionic contaminants such as Na and Cl ions and are particularly convenient for electronic units [183].

The method of forming zinc oxide light-shielding film for liquid crystals shields includes the injection of vapors of alkyl zinc compound with ozone or atomic oxygen in the activation chamber after which they pass through a chamber for ZnO film deposition at low temperature heating at about 473 K. The method is applicable for large scale production of these films [184].

An evidence for a new passivating indium rich phosphate prepared by UV/O_3 oxidation of indium phosphide, InP, is provided in [185]. The phosphate does not exist as crystal compound and its composition is $InP_{0.5}O_{2.75}$. The passivating ability of the latter with respect to InP surface is discussed.

To improve the light-absorption characteristics of oxide optical crystals they are heated in ozone-oxygen atmosphere [186, 187]. Thus the light absorption from the optical crystal in a wave range different from that with which the crystal affects its own absorption is reduced to the most possible level. Devices using such oxide optical crystals with improved absorption characteristics work with high efficiency as optical amplifiers, optical isolators, and optical recording medium or optical generators.

The manufacture of solar cell modules with transparent conducting film covered by amorphous Si layer and electrode on the backside linked to the transparent isolator layer is described in [188]. The preparation includes the application of a laser beam for electrode molding and exposure in oxidizing atmosphere containing 0.5–5 % O_3 or ≥10 % O [188].

A method for strong oxidation in ozone atmosphere is proposed for surface activation of photoconductive PbS films [189].

Adhesion-producing materials for electroless plating and printing circuits contain particles of thermostable material slightly soluble in the oxidizing agent; the particles are dispersed in the thermostable resin which becomes almost insoluble in the oxidizing agent at hardening. These materials find application for printing circuits and are treated by oxidizing agents (*e.g.*, chromic acid, chromate, permanganate, or ozone) to create a concave material surface [190].

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ГАЛУЗІ ЗАСТОСУВАННЯ ОЗОНУ

Анотація. *Показано, що сильна оксидаційна дія озону забезпечує базу для розвитку новітніх або модернізованих технологій, які широко використовуються в екології та різних сферах промисловості. Спеціальну увагу приділено очищенню відхідних газів, стічних вод та забруднених грунтів. Детально розглянуті процеси дезінфекції та очищення питної і технологічної води. Наведені приклади застосування озону в хімічній, фармацевтичній, парфюмерній, косметичній і целюлозо-паперовій промисловості, мікроелектроніці та ін.*

Ключові слова: *озон, екологія, промисловість, вода, гази, органічний синтез.*