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Crimean Agricultural Institute

Zelinsky Institute of Organic Chemistry, Academy of Sciences of the USSR

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PROGRESS IN THE STUDY OF THE AGING OF FIBROUS CELLULOSIC MATERIALS

G.N. Rozmarin

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1. INTRODUCTION

Cellulose is the most common natural organic substance and forms the basis of the cell walls in higher plants. Man uses vast quantities of cellulose (~ 500 million tonnes per annum) in the form of various fibrous materials; this tremendous consumption is compensated annually almost entirely by the process of photosynthesis [1,2].

Cellulose plays an important part in the national economy, and a number of organic manufacturing industries are based on the processing of this natural polymer; cellulose is used to prepare various types of paper, synthetic fibres, cotton fabrics, cine film, lacquers, explosives, etc.

The chief sources of cellulose are wood and cotton. Cellulose obtained from annual vegetation (flax, ramie, hemp, reeds, and straw from various grasses) is also of considerable importance. The technological process of cellulose production and purification may be accompanied by degradation resulting from processing. Certain necessary oxidising operations (for example, the pre-ripening of alkali cellulose in the manufacture of viscose rayon, bleaching, scouring, and dyeing) lead to undesirable and harmful consequences. The continuous degrading action of the atmosphere, heat, light, and moisture is shown spontaneously during the storage or exploitation of fibrous cellulosic materials, leading to premature wear and breakdown. All this introduces into the economy considerable losses, which exceed the losses due to the corrosion of metals [3].

In the chemistry of macromolecular compounds, the term *degradation* signifies the entire range of phenomena leading to a decrease in the length of the macromolecules. The decrease in the length of the molecular chains under the influence of internal or external factors takes place spontaneously and leads to *aging* of the polymer, that is, it leads to a decrease in the mechanical strength of the material and a decrease in its period of serviceability.

Degradation processes are usually complex, since it is difficult to determine the factors directly responsible; in general, these processes are brought about by the action of heat, light, and atmospheric oxygen. These factors operate simultaneously in the form of thermal, photochemical, and oxidative processes. There are several classifications of the different types of cellulose degradation [4,5].

Although the importance of the study of the mechanism of degradation is obvious from the practical and scientific viewpoints, many aspects of this mechanism have not been touched upon, despite the rising increase in the number of papers devoted to this problem. The degradation of cellulose leads to the formation of complex reaction products containing, in addition to the original hydroxyl groups, other non-hydroxyl functional groups produced as a result of oxidative degradation, and a certain number of broken units may be present together with unchanged elementary cellulose units: all these changes labilise the β-glucoside bonds of the chains and lead finally to a decrease in the length of the macromolecules.

In the study of the chemical changes, use is made of physical, physicochemical, and chemical methods, and also methods of artificial aging, in order to estimate the nature, direction, and intensity of the degradation processes, the durability of the manufactured products, the mechanisms of the reactions, etc.

The aim of the present review is to summarise the progress made in the recognition of the nature and mechanism of the processes involved in the degradation and aging of fibrous cellulosic materials, and also to point out the most rational methods for preventing the degradation of these materials.

2. THE DURABILITY OF PAPER

The durability of a fibrous material (paper, cardboard, cellulose fibres, or cotton fabric) is determined by its ability to withstand the action of the internal and external factors bringing about degradation during prolonged storage or under conditions of use, when the material is subjected to various mechanical treatments (folding, crumpling, elongation, etc.)[6]. The durability depends on the ability of the material to withstand the action of the surrounding medium, that is, the action of light, moisture, heat, and harmful atmospheres containing industrial gases. Decrease in the durability of fibrous materials, in particular paper, is usually accompanied by a decrease in the degree of whiteness.

Chemical analysis of the fibrous material (for example, paper) may give interesting information on its durability; the approximate period of resistance to wear shown by papers can be found from the data in Table 1.[7-9] Chemical analysis cannot always characterise the durability, however. For example, old Chinese papers (500–925 years old) and European documents (400 years old) have been found in good condition, although the α-cellulose content of these papers amounted to only 65–67%.[11] Thus other factors (for example, pH) play an important part.

The exceptional stability of papers manufactured in ancient times can be attributed to their preparation from an exceptional form of raw material (cotton or flax fibres or rags), the mild digesting conditions, the use of starch and gelatin for sizing, use of the minimum amounts of fillers, bleaching in sunlight, and drying under natural conditions. The change to the production of paper from wood cellulose, with mechanical processing on paper-making machines, led to a sharp decrease in the stability of the paper [12]. Modern forms of paper are not durable, and this is due not only to the use of fibres from wood cellulose but also to other technological factors.

The best method for estimating the durability of paper is apparently by *natural aging* under conditions of prolonged storage. This method is applicable to paper which is many centuries old; for modern papers, use is usually made of *artificial (accelerated) aging* methods, based on the fact that

TABLE 1. Estimation of the durability of papers from data obtained by chemical analysis [10].

Minimum period of use, a	Minimal α-cellulose content, %	Copper number	Minimal resin content, %	pH	Lignin
500	90	1.0—1.5	1.0	5	absent
100	80	2.0—2.5	1.5	5	absent
50	70	3.5—5.0	2.0	4.5	absent
Less than 50	no limit				present

damage to paper under natural conditions is due to the action of atmospheric oxygen, heat, and sunlight (direct or diffuse), the degradation being hydrolytic and oxidative in character. In artificial aging, the same factors as in natural aging are used, but under more severe conditions. The most important methods of artificial aging are given below[13-15].

1. Thermal treatment at 105° for 3 d in a drying oven with natural or controlled circulation of air.

2. Treatment with ultraviolet radiation.

3. Hydrolytic degradation in an atmosphere containing sulphur dioxide.

4. Oxidative aging in an atmosphere of oxygen at 15 atm pressure and 50–60°.

5. Aging in air with relative humidity 45% at 38° for 200 h.

6. Aging in air with relative humidity 75–80% at 30–40° for 45–180 d in the presence of definite quantities of oxygen and sulphur dioxide.

Irrespective of the method used, the change in the same physicochemical properties (tensile strength, number of double folds, elongation, bursting strength, etc.) and physicochemical properties (concentration of α-, β-, and γ-celluloses, degree of polymerisation, degree of whiteness, concentration of functional groups, etc.) is followed. Of particular importance is the determination of the degree of polymerisation (DP): the higher the molecular weight of the cellulose, other conditions being equal, the more stable the paper prepared from it.

The technological factors decreasing the durability of modern forms of paper include the following[16,17]: (1) the decrease in the DP resulting from digesting, beating, and bleaching; it is possible to develop operating conditions under which the change in DP will be a minimum; (2) sizing in acid medium (coagulation of rosin by aluminium sulphate); of considerable promise in this respect are neutral and alkaline sizing procedures, which give papers with increased durability[18,19]; (3) the addition of fillers, which may facilitate degradation processes, although they

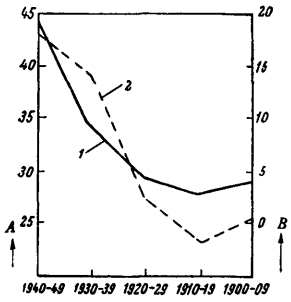


Fig.1. Comparison of the strength of modern printing papers prepared in the past 50 years.
A) Mean values of the resistance to tearing; 1) ditto.
B) Mean values of the resistance to folding; 2) ditto.
The values of the strength of modern papers, prepared in 1960, lie outside the diagram.

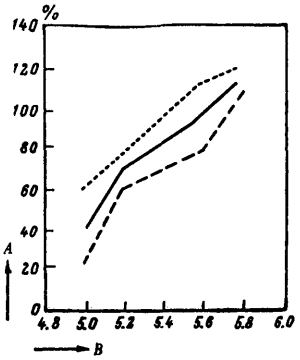


Fig.2. Effect of the pH of paper sheet on the decrease in strength under the influence of artificial aging.
A) Mean values of the resistance to folding as a percentage of the original values.
B) pH of cold aqueous extract.
The effect of artificial aging is equivalent to natural aging for 25 years. Photographic paper base was used.

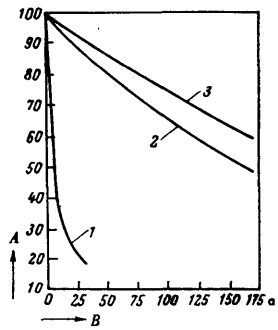


Fig.3. Comparison of the decrease in stability under the influence of artificial aging for old and modern printing papers.
A) Values of the resistance to folding as a percentage of the original values.
B) The durability of the papers (in years) established by artificial aging.
1) Modern printing papers wear rapidly; 2) the same papers treated with hydrogen carbonate solution; 3) mean value for seven old papers 250–400 years old.

may also, on the contrary, retard these processes[19]. The conditions necessary for the production of papers with increased durability have been described[20-22]. By using alkaline fillers, for example, $CaCO_3$, it is possible to reduce the acidity of paper and increase its durability (Figs. 1–3)[22].

Cellulose fibres can be arranged in the following order of decreasing stability[10]: (cotton, flax, hemp) > (sulphite and soda cellulose) > (esparto and straw) > (wood pulp).

The compositions used in paper manufacture are classified as follows[23] (in order of decreasing stability): (a) pulped rags (100%), (b) pulped rags (50%) + wood cellulose

(50%), (c) wood cellulose (100%), (d) wood cellulose + wood pulp (in different proportions).

Variations of different compositions using cellulose from annual vegetation (reeds and straw) have been put forward[24].

The durability of paper also depends on the conditions of storage and use[25]. Thus during storage, special measures are taken to protect papers from chemical[26], physical[27-29], or biological[30-33] agents.

The literature contains data on the appreciable depolymerisation of cellulose during bleaching, leading to a decrease in the stability of papers[34]. Uchastkina[35] and later Dixon and Nelson[36,37] developed equations for determining the relationship between durability and the physicomechanical characteristics of the original material. Finally, mention may be made of methods and apparatus for treating old papers for purposes of regeneration[38,39] or methods of chemical modification to increase resistance to heat and light[40].

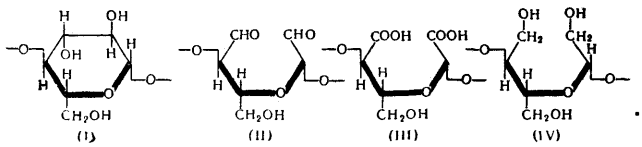
3. THE AGING OF FIBROUS MATERIALS

During storage and use, polymers show a continuous change in a number of variable properties — rigidity, elasticity, durability, and colour — usually referred to as aging[41]. In cellulosic materials, in particular paper, aging is accompanied by a decrease in the degree of whiteness (*yellowing*). The first quantitative observations were made as early as 1918.[42]

The sensitivity of cellulosic fibres to degradation depends on a number of factors. According to certain data[43,44], this is due to the presence of so-called "weak points" in the cellulose structure, appearing as a result of the stresses undergone by, for example, a single macromolecule taking part in the formation of two separate crystalline regions. The number of such weak points may be revealed by oxidative reactions and determined by chemical methods. According to other data[45], these stresses in cellulose appear as a result of repeated drying processes during the technological processing of the material, leading to the irreversible physical phenomena of aging (decrease in viscosity, physiocomechanical characteristics, sorption of dyestuffs, etc.). All these phenomena are described as *internal defects in physical structure*.

Another internal factor is the presence of *defects in chemical structure*. Ivanov and coworkers[46] attribute departures from the normal structure in cellulose to the presence of carboxyl and carbonyl groups, leading to the production of "weak points". Rånby[47] states that some of these non-hydroxyl groups appear as a result of chemical treatment, whereas a certain proportion (one group per 100 glucoside residues) are already present in the wood[47].

Other authors[48,49] have established the following order of stability of the elementary unit in cellulose in degradation processes, for functional groups of different kinds in positions 2 and 3:



The rate of hydrolysis increases in the order I < II < III < < IV.

Korshak and coworkers[50] showed that the resistance of polymers to degradation increases with increase in the length of the macromolecules.

Of the other main factors responsible for aging, *external factors* require emphasis. Cellulose is almost completely stable at room temperature in the dark[51], but with increase in temperature to 100–120° in the presence of air, oxidation processes begin to take place, the rate of these processes increasing in the presence of moisture[52]. Rheological determinations have shown that degradation takes place even at room temperature (the long-chain cellulose macromolecules disappear)[53].

Aging is also favoured by the fact that the weak points referred to above are extremely susceptible to the action of oxygen[54,55], oxidation taking place by a chain reaction[56]. The rate of hydrolysis of cellulose at these "weak points" is 300 times the rate of hydrolytic rupture of an ordinary β-glucoside bond; it should be borne in mind that one weak unit is found for every 400–500 anhydroglucoside units[57]. The rate of hydrolysis of wood cellulose is reduced considerably by preliminary treatment with sodium tetrahydroborate[58].

Mathematical equations describing qualitatively the effect of aging in various grades of paper under the influence of heat, light, or wear have been put forward[59-64]. The rate of these effects, including photo-oxidation or thermal oxidation, is determined by the temperature, the presence of atmospheric oxygen, light, ultraviolet radiation, etc. Thus characteristic features of photo-oxidation are the photochemical initiation of the reactions and the stability of the peroxides formed, whereas characteristic features of thermal oxidation are the chain reactions of peroxo-compounds formed under the influence of heat[65,66].

It has been shown for the example of rubber[67] that aging depends on the number of active reaction centres: degradation under the influence of ultraviolet radiation, despite the superficial nature of the irradiation, is much more intensive than the effect of heat, although with the latter the reaction takes place throughout the entire bulk of the polymer[68-70].

The phenomenon of keratinisation, manifested as a decrease in the reactivity of the fibres as a result of drying above 100°, is observed during the aging of cellulose. Keratinisation is attributed to merging of the fibrils to form characteristic aggregates, with subsequent bonding by hydrogen bonds, leading to a decrease in the physicomechanical characteristics[71,72].

The aging of various documents or books in libraries in large industrial cities results from the action of the atmosphere, which contains sulphur dioxide. Study of the absorption of sulphur dioxide by papers[73] shows that the reaction of this compound is catalysed by traces of heavy metal ions (Fe, Cu, Cr, V, Co, Ni, or Mn); Na, K, Ca, Ba, and Al ions have no catalytic action. A number of inhibitors (disodium hydrogen phosphate, 8-hydroxyquinoline, or ammonium oxalate) have been proposed for suppressing the action of these metals[74].

The influence of metal ions on the aging of papers has been studied by many workers. Stübchen-Kirchner[75] showed, for example, that the presence of the ions Fe^{3+} > > Fe^{2+} > Cu^{2+} causes yellowing of paper, whereas other ions stabilise the colour of paper, in the following order:

$Cd^{2+} > La^{3+} > Mg^{2+}$. Similar phenomena were observed by other authors [76-79], who emphasise the importance of iron ions in the formation of coloured complexes with rosin during sizing. Similar effects of yellowing in paper have been noted when gelatin and starch were used as sizing agents [80,81].

In the study of the yellowing of monocarboxycellulose under the influence of sodium, calcium, manganese, and aluminium salts, it was established [82] that the free carboxy--groups show a tendency to form anhydrides, lactones, and salts; the formation of salts intensifies the colour. Czepiel [83] arranged metal ions in the following order of decreasing action on the stability of the whiteness of papers: $Fe^{3+} > Fe^{2+} \geq Cu^{2+} > Al^{3+} \geq$ control specimen without ions $\geq$ $\geq Cd^{2+} \geq La^{3+} \geq Mg^{2+} \geq Mn^{2+}$. Manganese salts retard aging. Analogous results were reported by other authors [84-86]. Wultsch and coworkers [87] proposed preliminary treatment of the paper pulp with complex salts of the Trilon B or sodium polyphosphate type (in concentrations of 0.06–0.08%) to remove traces of metals (Fe, Cu, Mn, Co, Al, Cd, and Mg) and increase the whiteness of paper.

The yellowing of paper is an extremely undesirable phenomenon, particularly since paper with a high degree of whiteness can now be produced. The degree of yellowing is defined by the PC number (post colour number). [88] Most authors consider that yellowing is a natural consequence of the accumulation of carbonyl compounds in the cellulose or paper [88-99]. Okada and Ida [99] even established a direct relationship between the degree of yellowing and the quantity of carbonyl groups.

Sikhtol and Virkol [100] made a detailed study of the influence of various functional groups in cellulose on the phenomenon of yellowing, and established that: (1) a formyl group at $C_{(1)}$ in the elementary unit does not cause yellowing, whereas at $C_{(2)}$ and $C_{(3)}$ it favours this process; (2) hydroxyl groups in positions $C_{(2)}$ and $C_{(3)}$ do not cause yellowing; and (3) carboxy-groups in positions $C_{(2)}$ and $C_{(3)}$ bring about the same yellowing effect as formyl groups; the intensity of the yellow colour is greater when these groups are present in the form of the sodium salts, and weaker in the case of the calcium salts.

Sikhtol [100] points out that yellowing is accompanied by a decrease in the DP of cellulose and an increase in the value of the copper number; in the latter case, an increase in the copper number from 5 to 50 has no influence on the yellowing of such celluloses as sulphate cellulose, bisulphite cellulose, cotton cellulose, and hemicellulose.

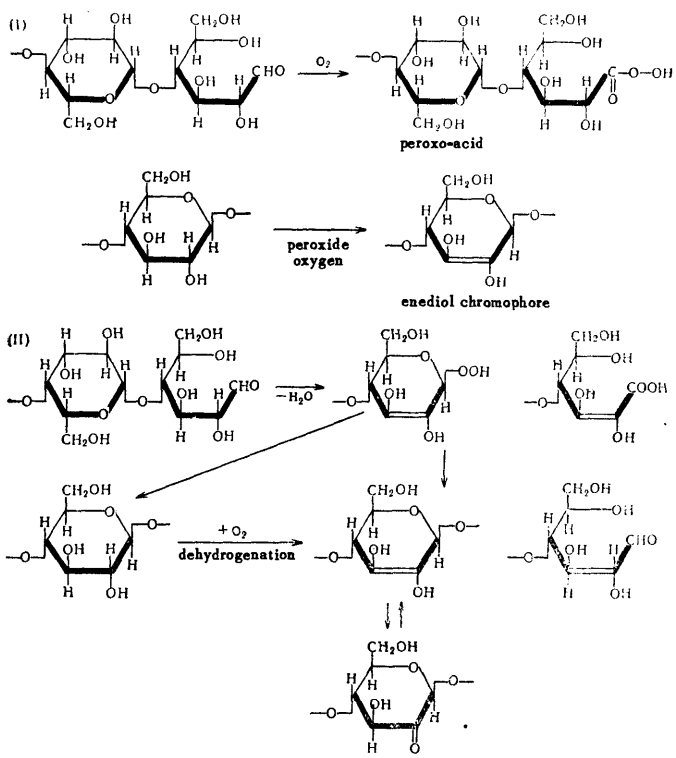
The yellowing of celluloses decreases with removal of the hemicelluloses, since the presence of the latter facilitates the hydrolytic formation of low-molecular-weight compounds of the oligosaccharide type or even monosaccharides, which condense under the influence of pectic substances and are converted into brown humic products [101-111]. Some authors relate the phenomenon of aging to the concentration of hemicelluloses [112] and, in particular, γ-cellulose [113].

Celluloses obtained by use of an ammonium hydrogen sulphite cooking liquor undergo yellowing more rapidly than those obtained using a calcium hydrogen sulphite liquor [114]. The stability of the whiteness may also depend on other technological factors, for example, the methods used to bleach the celluloses [115], the best results being obtained by bleaching with chloride dioxide [116]. In all, preliminary treatment with sodium tetrahydroborate can be used to increase the whiteness [117,118].

Roudier and coworkers distinguished two successive stages in the aging and yellowing of papers: (1) *hydrolysis* (as a result of chemical technological treatment or the action of moisture after preparation of the papers), and (2) *degradation* (which is more marked, the higher the concentration of hemicelluloses); the latter also leads to aging [119-122]. Similar conclusions were reached by other authors [123,124].

In an examination of the influence of soluble substances on the increase in the rate of aging of cellulose, Treffers [125] found, among the degradation products, organic acids which have a hydrolytic influence on the separation of hemicelluloses with the formation of free pentoses and oligosaccharides. Under the influence of the same acids, sugars are converted into dark humic products.

Here, mention must be made of an attempt by Kleinert and Marraccini [126] to establish the chemical mechanism of the aging and yellowing of celluloses under the influence of heat. They showed that peroxides are formed during aging [112]. In the presence of air (I), peroxo-groups and enediol compounds are formed, and in the absence of air (II), polyacetal groups are formed; in both cases unsaturated chromophoric groups are produced.



The individual stages of this mechanism were established chromatographically but the scheme is nevertheless fairly speculative.

A similar study was made of the aging of cotton cellulose in 0.5 *N* NaOH in the absence of air at elevated temperatures; the formation of saccharic acids was established chromatographically [127]. Under the influence of atmospheric oxygen and light, cotton cellulose shows a change in DP during ripening in the cotton-plant bolls under conditions of natural and accelerated aging [128]. Different mechanisms of degradation in the presence of oxidising agents of different types have been pointed out [129], together

with the unique part played by the carbonyl groups in this process [130].

In a comparison of natural aging (for 4, 8, 22, and 26 years) with accelerated methods (72 h at 100°), Wilson [131] found good agreement between the results obtained by the two methods for the change in the concentration of α-, β-, and γ-celluloses, the acidity of the aqueous extract, and the mechanical characteristics of the papers; he established that accelerated aging under the above conditions is equivalent to the effect of natural aging for 25 years. The method of artificial aging has also been used to study the durability of textile fibres [132]. The resistance of fibrous materials to aging is usually established by determining their viscosity [133]; no difference in the concentration of carbonyl and carboxyl groups has been observed for a given DP value [134].

Papers containing wood pulp undergo aging more rapidly because of the increased lignin content. There are reports of a direct relationship between aging and the lignin concentration [135-141]. The phenomenon of aging has also been studied for papers produced from linen and cotton rags [142] and also for papers prepared from wood and straw celluloses [143] or from jute [144]. In all, it was found that aging is accompanied by oxidative and hydrolytic reactions.

4. THE THERMAL DEGRADATION OF FIBROUS MATERIALS

Most work on degradation has been carried out by thermal treatment of the cellulose or paper. Yabrova [145] subjected newsprint to thermal aging (at 80° and 20° and a relative humidity of 60%) and observed a decrease in the number of double folds on the fifth day of treatment; at the same time, the solubility of the fibrous material in 7.4% sodium hydroxide solution increased, with a simultaneous increase in the concentration of carboxy-groups.

In a comparison of artificial aging (100° for 72 h) with natural aging, Royen [146] attributed the oxidative degradation of papers to the presence of hemicelluloses. Gluchowska and Winczakiewicz [147] equated the action of thermal treatment under these conditions for different grades of paper prepared from sulphite cellulose to only six years of natural aging (instead of 25 years, as is generally assumed). The presence of carboxy-groups in cellulose leads to a decrease in the heat-resistance of papers [148].

Simionescu and coworkers [19,149] studied the effects of artificial aging for more than 50 grades of writing, printing, and technical papers manufactured in various Roumanian factories, determined the most stable grades, and the technological factors favouring the production of durable paper. The addition, to the fibrous composition of the papers, of cellulose from annual vegetation (reeds and straw) in quantities up to 30–50% in mixtures with spruce cellulose did not lead to any significant intensification in the degradation; this is of practical importance for Roumanian conditions [150].

The most important factors influencing the heat-resistance of cellulose and papers are the DP, the molecular composition of the fractions, and the active acidity of the material; the most stable celluloses are cotton cellulose and sulphate celluloses, and the least stable are bleached (non-purified) sulphite celluloses [151]. The parameters most sensitive to the action of heat are the whiteness, viscosity, and number of double folds [152].

Sulphate cellulose has been shown to have a high heat resistance. In the case of bleached kraft cellulose, it has been established that there is a difference in the behaviour during artificial aging, depending on the temperature and the presence or absence of moisture [153]; other conditions being equal, the presence of lignin and hemicelluloses intensifies degradation [154,155]. Intermediate drying of cellulose for paper-making to a moisture content of 25% leads to a decrease in the mechanical characteristics of the paper [156]. Papers prepared from kraft cellulose, thanks to their heat-resistance, are better than the corresponding grades of paper prepared from rags [157-160], so that they are preferred for work on the restoration of documents [161] or for the production of capacitor papers [162-164]. Fabre [165] recommends chemical methods for the analysis of sulphate papers, in order to examine their aging in electrical transformers.

Cardboard becomes sensitive to the influence of heat only at a relatively high temperature (200°) [166].

Comparison of the aging of cellulosic fibres from cotton [167] or from artificial silk under the influence of heat with that for natural silk [168], and also comparison of the aging of natural fibres [169] with that of synthetic fibres [170], are of practical interest. The heat-resistance of fibres is increased by the addition of antioxidants [171]. In a study of the action of high temperatures (100–160°) on viscose fibres, Agster established that the following stages are involved in the degradation: up to 140° hydrolytic processes predominate, in the range 140–150° oxidative processes predominate, and in the range 150–160° thermal cracking begins [172,173]. At 145° the strength of viscose fibres decreases by 45% relative to the original value [174].

Interesting results have been obtained in the pyrolytic degradation of cellulose. Thus at 172°, [175] a number of gaseous products (CO, CO_2, and H_2O) were obtained, and saccharic acids, aldehydes, ketones, and glucose were determined by paper chromatography in the residue. In the presence of air, the reactions take place initially in the amorphous regions and then continue in all regions with a simultaneous decrease in the DP to a constant value [176]. At higher temperatures, for example, at 350–375°, a residue containing 55% water, 12.5% laevoglucosan, 15% carbonyl compounds, and 7.5% of various acids is obtained [177].

In the absence of air [178], the thermal degradation of cellulose takes place with an activation energy of the order of 26 kcal $mole^{-1}$. The pyrolysis of fibrous vegetable materials has been studied in the presence of mineral salts [179] under different temperature conditions [180-186]. In all, the formation of laevoglucosan with 1,5 and 1,6 oxygen bridges was established [187]. A relationship was established between the reactivity of celluloses and their behaviour during pyrolytic degradation [188]. In the degradation of cellulose with a molecular weight of approximately one million for 10 h at 130°, one chain unit in every 18 units underwent a change, even in the absence of air [189]. Analogous data on the degradation of various native celluloses have been given by other authors [190-193].

An important contribution to the study of various aspects of thermal degradation has been made by Golova and coworkers. On the assumption that β-glucose is an intermediate product in the formation of laevoglucosan [194,195], they showed [196] the possibility of the direct formation of the latter from cellobiose [197,198], pectic substances [199], and polygalacturonic acids [200] by splitting at the 1-4-β-glucoside

bond and isomerisation of the chain fragments. The yield of laevoglucosan depends on the original structure of the cellulosic material[201], high yields being obtained where the density of packing of the molecular chains is high. Similar conclusions were reached by other authors[202,203].

The extent of degradation depends not only on temperature but also on the duration of treatment, the degree of polymerisation of the cellulose, and the composition and nature of the medium in which the degradation takes place. For example, moderate heating (up to 120°) is accompanied by depolymerisation, but at elevated temperatures (240°) dehydration begins with a subsequent change in the chemical composition of the elementary unit[204].

A review by Sergeeva[205] gave data obtained in a study of the changes and degradation undergone by wood vegetable fibres, and also the macromolecular components of wood, under the influence of thermal treatment. In particular, it was reported that the degradation of the cell walls of holocellulose takes place in stages: degradation of the hemicelluloses and the loose regions of the cellulose takes place at 155–260°, degradation of the secondary layer of cellulose begins at 280–285°, and at 280–300° the secondary layer of cellulose decomposes completely and degradation of the cellulose of the cambial layer begins; under these conditions, only the cellulose of the tertiary layer remains stable.

The degradation of cellulose has been carried out in various liquid media. For example, cellulose has been heated in petrol, benzene, pyridine, dioxan, and various alcohols, for 3 h at 200°; a decrease in the DP was observed[206]. Depolymerisation is more extensive in non-polar liquids (kerosene, benzene) than in polar liquids[207-209]. Heating for 1 h at 240° in anhydrous glycerol leads to an increase in the density of packing of the cellulose (the density of the specimen changed from 1.531 to 1.551). This led Sharkov and Shchleglova[206] to establish a direct relationship between the changes in the density of cellulose specimens and the changes in the infrared spectra of the specimens in the range 3000–3600 cm^{-1}. Usmanov and coworkers[210] established that thermal treatment of cotton cellulose leads to a decrease in the integral heat of wetting, and that a unique type of structural change takes place, leading to an increase in the ability to undergo changes in packing and an increase in molecular packing. The action of pure water on cellulose at elevated temperature has also been studied[211,212]; on treatment with water, the concentration of carboxy-groups increases, the water becomes acidic, and the cellulose undergoes extensive depolymerisation.

Degradation has been carried out in sodium hydroxide solutions at 170°,[213,216] sodium hypobromite solutions[214], liquid paraffin, superheated steam, sulphuric acid, and salt solutions in the range 130–250°, in order to establish the approximate mechanism of degradation[217].

The changes undergone by cotton cellulose during thermal degradation were described by Aubry[218]. Thus at 90° there is a moderate decrease in such parameters as the moisture content, mechanical strength, degree of whiteness, and DP, after treatment for only 4 h; at 110° these characteristics also decrease slightly (from the start in this instance), the rate of decrease in these characteristics increasing considerably only at 130–150° (the DP decreases from 3000 to 1200); the same rates are observed for the change in solubility in sodium hydroxide, the acidity of the aqueous extract, the copper number, the degree of whiteness, and the concentration of carboxyl groups in the cellulosic material. Hydrocellulose is distinguished by an increased heat-resistance; this is attributed to a difference in the number of "weak points" (one per 1000 glucoside residues for cotton fibre and one per 500 or 250 glucoside residues respectively for hydrate cellulose)[219-221].

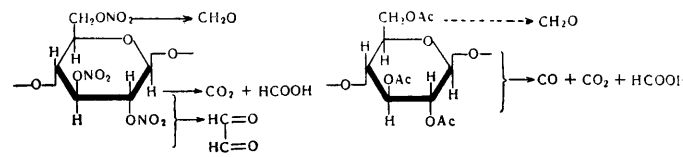
Significant changes are also observed in the X-ray diffraction patterns for native and mercerised cellulose as a result of thermal treatment; at moderate temperatures there is a change in the reflections corresponding to the (002) planes, and the (101) and (10$\bar{1}$) planes show irreversible broadening; in the case of cellulose-II the reflections of the (101) plane show gradual fogging[222]. At 300° the texture of both celluloses disappears completely from the X-ray diffraction patterns[224].

When the degradation of cellulose is carried out by increasing the temperature gradually (5.5 deg min^{-1}), dehydration is observed at 200–230°, and at 300° the water is removed completely and structural changes begin, with partial loss of carbon; above 300° combustion begins, with partial decarbonisation and formation of amorphous carbon[224].

The thermal decomposition of cellulose in a vacuum is accompanied by the production of carbonyl and carboxyl groups, with a simultaneous change in elemental composition[225]. Structural changes resulting from thermal treatment have also been described for mercerised cellulose[226,227].

The method of thermal degradation has been extended to cellulose derivatives. Thus the thermal decomposition of nitrocellulose[228,229] (which takes place by a chain reaction), cellulose acetate[230-234], ethylcellulose[235], or cellulosic fibres thermostabilised by partial acetylation[236] or cyanoethylation[237-239] has been described. Acetylcellulose was found to be more stable under conditions of thermal aging than other derivatives, its thermal stability being several times that of cellulose[240].

The thermal decomposition of nitrocellulose leads to the formation of oxides of nitrogen, volatile organic substances, carbon dioxide, carbon monoxide, formic acid, formaldehyde, glyoxal, and hydrogen cyanide[241]. On the basis of data obtained using tracer atoms, the following schemes were proposed for the degradation of cellulose nitrate[100] and cellulose acetate[235]:



It should be emphasised that in the last scheme the degradation products appear chiefly as a result of the rupture of the pyranose ring, and not by removal of the acetyl (Ac) groups of the macromolecule, as was previously generally accepted.

Thermal degradation, as a method of studying the structure of cellulose, provides extensive factual material and gives additional information on the overall mechanism of the decomposition. Different versions of the method are still used by many authors.

5. THE PHOTOCHEMICAL DEGRADATION OF CELLULOSE

During use, cellulosic materials always undergo aging under the direct influence of *sunlight.* Diffuse light (day--light, the light from "white" incandescent lamps or fluorescent sources) also leads to aging, although it rarely contains appreciable proportions of the ultraviolet range of the spectrum [242,243].

The influence of sunlight on cellulose fibres during the bleaching of flax and hemp in bleaching greens has been known for long: this action was attributed to the influence of heat and light [244,245]. The prolonged action of sunlight on various grades of paper (exposure for 5-120 d) produced different changes in the concentration of α-cellulose and in the value of the copper number [246,247]. Yellowing has been attributed to the presence of rosin size [248-251]. The bleaching of paper under the influence of sunlight filtered through window-glass has also been noted [252]. The aging of papers from bisulphite bleached and unbleached celluloses exposed to sunlight depends on the concentration of lignin present [253]. Since the spectrum of sunlight contains radiation with wavelength from 290 mμ to 700 mμ, it should be noted that cellulose absorbs radiation with $\lambda < 400$ mμ; [254,255] the presence of lignin [256-259] displaces the absorption to the range 280–400 mμ; the use of rosin as size intensifies the absorption in the range 330–440 mμ. [260]

Marini [261] compared the action of sunlight in the yellowing of papers with that of illumination by a mercury lamp; the results of exposure to the two different light sources are different, due to the difference in the energy distribution of the spectra. Analogous experiments were carried out by others [262].

Photochemical degradation is generally studied using *ultraviolet irradiation.* Under the influence of this illumination, simple sugars decompose with the formation of volatile products. Fructose [263] gives carbon dioxide, carbon monoxide, formaldehyde, methanol, and various acids; aqueous solutions of glucose and fructose gave carbon monoxide, methane, hydrogen, carbon dioxide. The rate of decomposition of fructose is seven times that of glucose [264]. In the case of cellulose irradiated in a vacuum (λ = 253.7 mμ at 40°), liberation of a gas mixture with characteristic composition (87.5% H_2 + 8.2% CO and 4.3% CO_2) is also observed; [265] depolymerisation (DP 1710 → 690) and an increase in the concentration of nonhydroxyl functional groups takes place simultaneously. The degradation is attributed to the conversion of alcoholic groups into carbonyl groups, accompanied by the liberation of hydrogen: a stoichiometric relationship was established between the number of broken glucoside bonds and the number of carboxy-groups.

The effects of ultraviolet irradiation on cellulose and paper depend on the wavelength. Irradiation with narrow ranges of the ultraviolet spectrum established a difference between the behaviour of papers with high lignin content (from wood pulp) and that of papers containing almost no lignin. Liberation of gases was observed always [266]; after an interval, the liberation of gases stopped, as a result of the screening effect of the carbonyl groups [267]. Radiation with wavelength 290–395 mμ was most effective [60,268]; according to data obtained by other authors, the active radiation is displaced towards 250 mμ. [269] A systematic study by Spinner [270] of the dependence of the degradation on the spectrum of the ultraviolet radiation showed that a unique part in the photodegradation is played by lignin, the moisture content of the medium, atmospheric oxygen, and the temperature of the medium. The phenomena of photolytic after-effects are also observed. These data are given in Table 2.

Emphasising the importance of physical bonds between the components of paper for the development of durable grades, Richter and Wells [273] developed a method of artificial aging by ultraviolet irradiation. Ultraviolet radiation was also used to determine the degree of decomposition of sulphite and sulphate celluloses and to establish the nature of fillers and contaminants [274].

McClaren and coworkers [275] studied the action of ultraviolet radiation (λ = 253.7–365.4 mμ) on paper prepared from bisulphite kraft celluloses, and established that rapid yellowing of the specimens takes place in the initial stages of exposure. A curious feature is that according to the results of these authors, the behaviour of the materials is independent of the humidity of the atmosphere or the presence of carbon dioxide or sulphur dioxide; the effect of exposure is restricted to a depth of 0.15 mm. According to the results of other authors [276], the light sensitivity of paper depends on the method of bleaching: papers bleached with sodium tetrahydroborate were found to be most stable, and celluloses bleached with calcium hypochlorite were found to be most sensitive to the action of heat and light.

The light sensitivity of bleached celluloses is closely related to the nature of the fibrous raw material, the method of digestion, and the use to which the material is put. Rozmarin and Simionescu [277] studied the chemical changes undergone by different celluloses under the influence of ultraviolet radiation, and established that for chemical celluloses the concentration of α-cellulose decreases with a marked increase in the concentration of hemicelluloses and a simultaneous decrease in the degree of whiteness. It was noted that the rate of formation of keto-groups is greater than the rates of formation of aldehyde and carboxyl groups. Papermaking grades of cellulose show an approximate analogous change in chemical composition. The degradation of cellulose from beech and reeds is more intensive than that of cellulose from spruce.

Spectroscopic study of photodegradation confirmed these conclusions; under the influence of ultraviolet radiation, cellulose and its derivatives undergo chemical and structural changes (new absorption bands due to carbonyl groups appear in the range 1720–1760 cm^{-1}, and the 3400 cm^{-1} band corresponding to the hydroxyl groups is displaced towards smaller wave numbers). These results also show that the oxidative changes involve the direct participation of atmospheric oxygen [277].

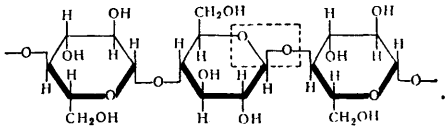
Cellulose can be regarded as transparent to radiation with $\lambda > 200$ mμ. Carboxy-groups absorb radiation of

TABLE 2. Influence of ultraviolet irradiation on cellulose.

Wavelength of radiation λ, mμ	Action on cellulose or paper containing no lignin	Action on cellulose or paper containing appreciable quantities of lignin	References
200–300	*Yellowing*: the presence of water inhibits the process; yellowing may begin during the after effect; temperature has no direct effect on the process	*Yellowing*: more intensive in the presence of air, moisture, and heat; moderate in their absence	266, 267
300–400	*Bleaching*: appreciable in the presence of moisture and air; heat causes yellowing	*Yellowing*: bleaching takes place in the absence of moisture and heat	258, 268, 271, 272
400–500	–	Bleaching may take place	258, 270

very short wavelength, whereas the C–O–C group does not absorb radiation with $\lambda > 220$ mμ.[278-280] Sippel[60] established that the energy corresponding to radiation with $\lambda = 350$ mμ, equal to 82 kcal mole^{-1}, is quite sufficient for the rupture of chemical bonds in polymers. It has been established that other wavelengths also correspond to appreciable energies[281].

From the above data it follows that the splitting of the $C_{(1)}-C_{(2)}$ and $C_{(1)}-O$ bonds of the elementary unit of cellulose may take place in different ways under the influence of ultraviolet radiation. Chromatographic determination of the corresponding cellulose degradation products confirmed, in particular, the mechanism of labilisation of these bonds, as shown below[282]:



By measuring the polydispersity, Page[283] proved that significant changes are undergone by cellulose subjected to ultraviolet irradiation for a prolonged period (500–2000 h). Recently, Rozmarin and Simionescu[284] established that appreciable changes take place in the polydispersity of celluloses as a result of shorter exposures (100–240 h); in all cases the maximum of the differential molecular-distribution curves was displaced towards lower DP values (papermaking celluloses acquire a more regular molecular composition under the influence of irradiation, but chemical celluloses, with more regular initial fraction composition, show a much greater increase in the degree of polydispersity). These changes are illustrated schematically in Fig. 4.

The above data confirm the theory (put forward as early as 1943[285]) that photolytic splitting of the cellulose chains takes place under the influence of ultraviolet radiation, with simultaneous photo-oxidation phenomena[286]. On the other hand, for cellulose and its derivatives, Tichener[287] found no relationship between the polydispersity and the course of the photolytic reactions.

Photochemical degradation involves free-radical chain reactions[288]. This was proved for cellulose by Simionescu and Poppel[289], who observed that solutions of hydroquinone and gallic acid inhibit the photodecomposition completely; this revealed that the reaction involved free radicals[19,290]. Zapol'skii[291] also confirmed this suggestion for the case of Cellophane, on the basis of spectroscopic data.

A mathematical method has been developed for calculating the number of cellulose chains split during photolysis from the concentration of aldehyde groups formed and the quantity of hydrogen liberated during the reaction[292].

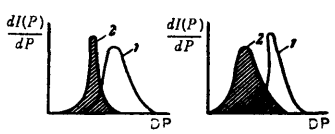


Fig. 4. Change in the molecular composition of paper-forming (left) and viscose (right) celluloses under the influence of ultraviolet radiation.
1) Control specimens; 2) irradiated specimens.

Flieder[293] used the ultraviolet light from bactericidal lamps to bleach old papers, and Belaya[294] used the same light to determine the durability of grades of paper used for printing. Simionescu and Poppel[295,296], on the basis of the artificial aging of papers by ultraviolet irradiation, recommended the use of kauri gum for the preservation of papers. A large number of versions of new methods of bleaching, using chlorine dioxide, sodium tetrahydroborate, sodium peroxide, and hydrogen peroxide, have been proposed, to increase the stability of the whiteness of papers[297] and reduce the effects of photodegradation[298,299].

Centola[300] established the following order of photo-stability for cellulosic materials: cotton > flax > hemp > > jute and linter > spruce viscose cellulose > spruce papermaking cellulose > spruce cellulose > sulphate cellulose > spruce semi-chemical cellulose > straw cellulose.

Using the numerical criterion of Geller and Meskin[301] for determining the degree of polydispersity, Rozmarin and Simionescu[284] gave another version of the order of photo-stability of bleached celluloses: spruce papermaking kraft cellulose > spruce bisulphite papermaking cellulose > > viscose sulphate cellulose from reeds > papermaking sulphate cellulose from reeds > viscose bisulphite spruce cellulose.

It has been shown that lignin facilitates the photodecomposition of cellulose, although it has also been reported[302] that lignin is able to retard oxidation processes. Papers sized with natural rosin are less stable to the action of light than papers sized with completely saponified rosin[303]. No appreciable yellowing effect is observed for cardboard[304].

Titanium dioxide fillers have a catalytic action. Atomic oxygen is formed, according to the reaction[305]:

$$2TiO_2 + h\nu = Ti_2O_3 + O,$$

and this oxidises hydrated cellulose[306] or cellulose derivatives[307] (for example, acetate rayon) preferentially. Under the influence of ultraviolet light, titanium dioxide acts an an oxidising agent on disaccharides (maltose, lactose, saccharose, and cellobiose) with the formation of the corresponding acids, but no splitting of the heterocyclic rings or acetal bonds was observed[308].

The presence of hemicelluloses and oxycelluloses does not play any significant part in the photolytic yellowing of cellulose from jute[309,310].

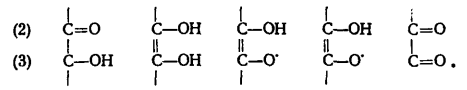
Zinc oxide increases the sensitivity to photochemical reactions, but glycerol, glucose, benzidine, etc. have a retarding influence[302]. More than 1% titanium dioxide may exert a protective influence on cellulosic materials[311-313]. A catalytic action is shown by Fe, Cu, Cr, Mn, U, Ti, and Mg ions[314]. Similar observations were made for synthetic[315,316] and artificial[311-313] fibres and on mixed fibres from cotton and Lavsan [Dacron, Ed. of Translation)][317].

Mention must be made of work on the influence of photodecomposition on the formation of cellulose ethers[318], which established a decrease in the reactivity of cellulose and also work on cellulose nitrate[319-321] and cellulose acetate[322].

Various schemes for the mechanism of the photodecomposition of cellulose have been proposed. Mention has already been made of the theories of Wilson and coworkers[265-267], Beelik and Hamilton[282], and Simionescu and coworkers[18,19,277,284,289,296]. In the opinion of these authors, ultraviolet radiation has a *photolytic* action on

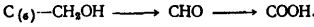
the bonds formed by the carbon atoms in positions 1 and 2[282] and an *oxidative* action on the carbon atoms in positions 2, 3, and 6[265,277]. The reactions take place with the participation of atmospheric oxygen[277] by oxidative chain reactions[19,289].

Work by other authors has confirmed these suggestions. Schurz and coworkers[323] studied the ultraviolet absorption spectra of the soluble products of the yellowing of celluloses and found the following chromophoric groups in positions 2 and 3 of the elementary unit:

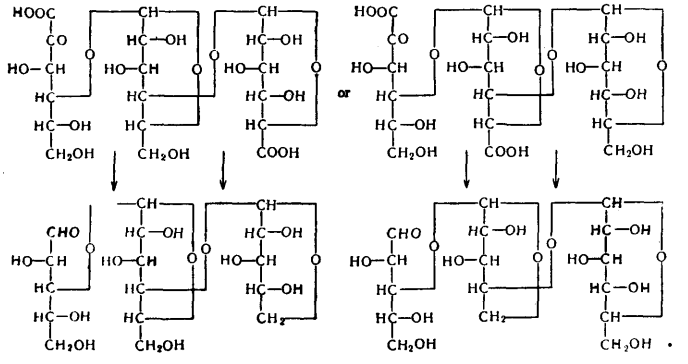


These groups undergo a number of changes, leading finally to splitting of the $C_{(2)}-C_{(3)}$ bond and the pentylene oxide bond 1–5 with the formation of brown products.

Zapol'skii[324] subjected Cellophane to the action of ultraviolet light and established an increase in the concentration of carboxy-groups as a result of the oxidation of primary alcoholic groups. On the basis of a study of the infrared absorption spectra, he suggested the following mechanism of photodegradation:



On the basis of data obtained by chromatographic separation of the products of the photodecomposition of cellulose, Bera and coworkers[325,326] concluded that cellulose decomposes to monosaccharides (xylose, arabinose, and glucose), cellobiose, and oligosaccharides (cellotriose and cellotetrose), which are converted into simple sugars by decarboxylation and splitting of the glucoside bonds:



The formation of xylose, arabinose, and glucose proves that photolysis of the β-glucoside bond takes place initially; the products are oxidised by atmospheric oxygen and decarboxylated under the influence of irradiation. It is difficult, however, to explain the formation of dark brown decomposition products by this scheme.

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The above published data indicate the considerable interest shown by scientists in the study of the degradation of cellulose under the influence of a variety of factors. The phenomenon of aging, which accompanies degradation processes, has also attracted the attention of research workers. Examination of the above results makes it possible to determine the progress made in each branch of the study of the degradation of cellulose and to establish the nature of the problems requiring further examination.

It follows from this review that in thermal degradation and photodegradation, cellulose exhibits dual behaviour: oxidation and depolymerisation. The heat- and light--stability of cellulosic materials depends on the nature of the cellulosic raw material, the processes of digestion and bleaching, and the conditions of use. It may also be taken as established that the two types of degradation (under the influence of heat and light) differ essentially only in the superficial action of light and the bulk action of heat. In both, the decomposition involves chemical changes in the cellulose macromolecules (under the influence of atmospheric oxygen or the oxygen atoms of the molecules itself) and rupture of the chains.

The mechanisms proposed by different authors for the decomposition of cellulose have thrown light on a large number of individual aspects of the chemical changes undergone by cellulose but all possibilities in this field have not yet been exhausted. In the solutions of these problems, use must be made of the more promising methods of study, for example, chromatographic and spectroscopic methods.

Among methods leading to an improvement in the durability of cellulosic materials, particular attention should be paid to the development of milder conditions for the technological processes involved in the preparation, purification, bleaching, and finishing of cellulose. Mention may be made, for example, of the harmful effects of beating, bleaching, and sizing in acid medium in the manufacture of paper. Methods involving the addition of various inhibitors to prevent the degrading action of air, heat, and light, and also methods for the chemical partial modification of celluloses[327] appear promising.

Finally, it should be noted that in the study of artificial aging, the contradictory results which have been obtained can be attributed to the fact that the conditions of humidity and temperature have not been strictly controlled. In this field it is necessary to determine the factors responsible for the decrease in the whiteness of cellulosic materials, to develop standard methods of accelerated aging, and to establish the part played by non hydroxyl functional groups. In this connection the development of accurate methods for determining the different functional groups of cellulose is of considerable importance.

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Department of Natural and Synthetic Macromolecules, Iasi Polytechnical Institute, Roumania

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THE PHYSICOCHEMICAL PROPERTIES OF OXYETHYLATED NON-IONIC SURFACE-ACTIVE SUBSTANCES

I. A. Gritskova, R. M. Panich, and S. S. Voyutskii

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I. INTRODUCTION

The production of non-ionic surface-active substances (NSAS) began in 1929–1935, when for the first time products were obtained by the addition of ethylene oxide to organic compounds containing at least one reactive hydrogen atom, such as the higher aliphatic acids, their amides, higher aliphatic alcohols, thiols, alkylphenols, amines, etc. These products are characterised by the number of ethylene oxide groups attached to one mole of the organic substance. It should be noted that the oxyethylene chains in the compounds are almost never of equal length, their distribution with respect to dimensions being described by a classical Poisson curve[1,2]. At the present time, methods are available for separating a mixture of polymer-homologues into individual products[3] and also for obtaining certain individual NSAS using particular chemical reactions[4].

As a result of the slightly hydrophilic character of ethylene oxide, the addition products usually have a higher solubility in water than the original substances. A significant advantage of oxyethylated substances is the possibility of controlling their hydrophilic nature by altering the quantity of attached ethylene oxide, and also the number of carbon atoms in the hydrophobic chain. This makes it possible to obtain substances with optimal properties for any given field of application. Another important characteristic feature of oxyethylated substances is that they cannot form salts, so that they are stable in hard water and can be used in combination with both anion-active and cation-active SAS.