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Zelinskii Institute of Organic Chemistry,
USSR Academy of Sciences

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THE PHOSPHORYLATION OF CELLULOSE

E.E. Nifant'ev

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I. INTRODUCTION

Although a large number of monographs and reviews have been published on the chemical modification of cellulose, questions associated with the phosphorylation of this important polysaccharide are treated superficially and incidentally in them, or even omitted altogether, as has been done in the latest treatise on the chemistry of cellulose [1].

The task of the present paper is to fill the gap: it represents the first attempt to collect together all the information on methods of preparation as well as the properties and practical application of phosphorus-containing derivatives of cellulose. The paper summarises investigations on the phosphorylation of cellulose, made mainly during the past thirty years, recent progress being reported in the greatest detail. A special place is given to describing the achievements made in the practical application of phosphorus-containing cellulosic materials.

The large amount of experimental work on the preparation of phosphorus-containing cellulose derivatives can be divided into two groups, according as phosphorylation is effected with derivatives of acids containing quinquevalent or tervalent phosphorus. The first group is in turn divided into two subgroups, the first of which comprises

papers on procedures for the direct phosphorylation of the polysaccharide, i.e. the replacement of the hydrogen atoms of hydroxy-groups by phosphorus-containing acid radicals; the second subgroup contains other methods for the chemical bonding of phosphorus to the macromolecular chain (indirect phosphorylation). A large number of papers and especially patents are devoted to the problem of conferring particular properties on cellulosic materials by impregnating them with compositions which include phosphorus compounds. In the latter case the formation of chemical bonds between cellulose and the phosphorus component has not in general been established, and therefore this question is not discussed in the review†.

The large number of publications on the preparation of phosphorylated celluloses is due to the growing technical interest in them. An important application of these products is the production of non-flammable textiles. The introduction of phosphorus into cellulose confers on articles made from it the ability to withstand the action of a flame‡. Cloth made from phosphorus-containing cellulose and clothes manufactured from it can be employed in firefighting, in furnace work, in the army, etc. [2-16]. Phosphorus-containing celluloses are used in several cases in the production of shrink-resistant [17] and crease-resistant [18,19] fabrics, which are resistant to water [8,20,21] and possess antiseptic [20,22] and rotproof [21,23,24] properties.

Phosphorylated celluloses are novel, as yet little studied, but promising ion exchangers. Their desirable properties are their hydrophilic character, in some cases high selectivity of ion-exchange action, and characteristic physical properties. In contrast to most other known adsorbents, these substances may be in the form of powders, wadding, or sheets, and are therefore employed in different ways in the ion-exchange process. They are used not only in the form of columns but also in other ways: thus a very promising procedure at the present time is continuous ion exchange by means of an endless belt of phosphorylated cotton [25]. The use of phosphorylated celluloses has been recommended for the isolation of Th^{4+}, Ti^{4+}, U^{4+}, Ce^{4+}, Fe^{2+}, ZrO^{2+}, UO^{2+}, Hf^{2+}, Cu^{2+}, and other ions from synthetic and technical solutions [22,25-46].

In some cases these esters are employed in radiometric instruments for the control of waters containing small concentrations of radioactive elements [47]. References have also appeared to the use of cellulose phosphates for the purification and separation of proteins, vitamins, and other important natural products [48-55].

Phosphorylated celluloses are fairly efficient cation exchangers: the ion-exchange properties of these compounds and other ion exchangers of similar type are compared in the accompanying Table [37].

Ion-exchange processes have been studied mainly with cellulose specimens containing acid phosphate groups, which, as is well known [56-58], are not always the most suitable for bonding a particular ion. Phosphonates, phosphoramidates, and phosphonamidates of cellulose have not yet been assessed from this point of view, which reveals certain prospects for the preparation of novel polymeric complexing agents. The usefulness of such researches is supported by the appearance of papers on the application to ion exchange of celluloses which have been impregnated with certain phosphorus-containing extractants for metals [59-61].

TABLE.

Ion exchanger	Exchange capacity, mg-equiv. g^{-1}	pH at half capacity
Cellulose phosphate, 1st H atom	1.3	1.5
Cellulose phosphate, 2nd H atom	2.6	7.5
Sulphoethylated cellulose	0.5	0.5
Carboxymethylated cellulose	0.3	3.7
Diethylaminoethylated cellulose	0.3	7.7

Phosphates and phosphonates of cellulose are of interest to several investigators concerned to establish a relationship between the physicochemical characteristics of substances and their structure [62,63].

II. PHOSPHORYLATION OF CELLULOSE BY DERIVATIVES OF ACIDS OF QUINQUEVALENT PHOSPHORUS

1. Phosphorylation by Acid Chlorides

The most widely used method for preparing esters of phosphorus acids is the reaction of alcohols or their alkoxides with the corresponding acid chlorides [64,65]. Several variants of this process have been used for the phosphorylation of cellulose. Work was published in 1932 on the reaction of cellulose with phosphorus oxychloride in the presence of phosphoric acid with and without a solvent present, a highly degraded, water-soluble product being obtained [66]. A less degraded material is obtained by employing cellulose which has first been treated with alkali [26,49,67-70], a water-insoluble phosphate being formed when the reaction is conducted in absolute benzene [26].

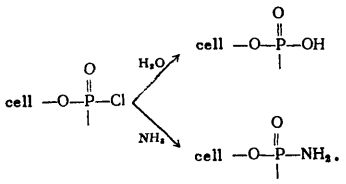
Much attention has been paid to the phosphorylation of cellulose with phosphorus oxychloride in the presence of ammonia [71] or pyridine [25,27,35,72,73], when a polysaccharide containing rather more than 9% of phosphorus could be obtained (the phosphorus content was somewhat higher when hydrocellulose was used [27]). Under the conditions of esterification, partial replacement of the hydroxy-groups of the polysaccharide by chlorine is observed [25]. Phosphorylation in the presence of pyridine is also accompanied by considerable degradation of the product. Thus the preparation of a cellulose phosphate containing 3.5% of phosphorus involved a loss of strength of 50%, and the loss increases with rise in the phosphorus content [27]. There are indications that, in the presence of pyridine, phosphorus oxychloride will phosphorylate derivatives of cellulose, e.g. ethyl- and hydroxyethyl-cellulose and cellulose acetate [27,73].

Treatment of cellulose with phosphorus oxychloride yields mainly phosphorochloridates, apparently consisting mainly of Cell–O–$POCl_2$ residues [27]. The lability of the chlorine atoms in these compounds corresponds to that in ordinary alkyl (or aryl) phosphorochloridates [64,65]. They are exchanged for hydroxyl on treatment with water, and

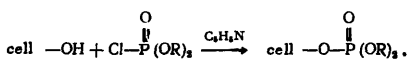
† Detailed accounts of the modification of the properties of cellulose by impregnation with phosphorus-containing compositions will be found in several monographs [2-4].

‡ Several theories have been put forward to explain from various points of view the non-combustibility of phosphorylated celluloses [2,4,5].

for an amino-group with ammonia, cellulose phosphates and phosphoramidates respectively being formed[70]:



Cellulose is phosphorylated also by alkyl (and aryl) phosphorochloridates in the presence of tertiary amines[10,74-79], when mixed phosphoric esters are formed, e.g.



Derivatives of cellulose undergo similar reactions[73,80].

References have recently appeared to the possibility of the phosphorylation of cellulose with phosphoramidochloridates[81] and with phosphonochloridates[76,77,81-83], the products containing fragments in which phosphorus–carbon and phosphorus–nitrogen bonds are present. Phosphoramidochloridates obviously phosphorylate cellulose partly also by a mechanism involving alcoholysis of phosphoramidates[81].

The interaction of cellulose with polyphosphonitrilic chlorides in the presence of pyridine has been described[19,84], but there is no rigorous evidence of the formation of macromolecular glycosylphosphonitriles.

2. Phosphorylation by Acids

At ordinary temperatures cellulose hardly reacts at all with phosphoric acid, but only swells and partly dissolves in it[85,86]. Nor are cellulose phosphates obtained on heating, owing to degradation of the polysaccharide[87,88]. Unsatisfactory results have been obtained also for phosphorylation with phosphoric acid in the presence of sulphuric acid[89] or of phosphorus pentoxide[90], only water-soluble oligomers being obtained in these cases. An only slightly degraded product containing a few per cent of phosphorus was obtained by Ermolenko and Kaputskii, who acylated cellulose with phosphoric acid (0–10°), the reaction being activated with oxides of nitrogen[91,92]. These workers consider that macroradicals are produced by the action of nitrogen dioxide on cellulose, and it is these which are responsible for phosphorylation.

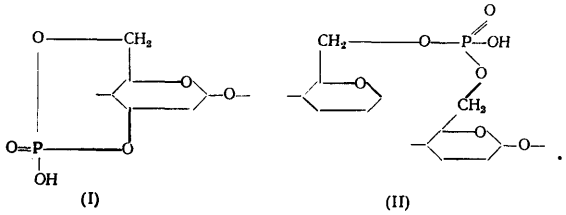
Considerably better results were obtained for the phosphorylation of cellulose with phosphoric acid in the presence of ammonia and other compounds containing nitrogen. The reaction is often conducted under relatively mild conditions, and in several cases it is possible to obtain cellulose phosphates with little degradation. The addition of nitrogenous bases is necessary to neutralise the phosphoric acid, and consequently to diminish its dehydrating effect. It is possible that urea increases the reactivity of cellulose, since the latter is known to be able to change its supermolecular structure under the influence of nitrogeneous bases[93].

The esterification of cellulose with phosphoric acid in the presence of urea was first accomplished towards the end of the 1930s[6,94]. A large (mainly patent) literature then appeared on new variants of the phosphorylation of cellulose with phosphoric acid in the presence of amines, urea, dicyanodiamide, melamine, guanidine, formamide, and other compounds containing nitrogen[6,8,16,18,20,31-34,37,39,95-120]. It has recently been proposed to conduct the process also in the presence of 2-alkoxyethanols and sulphonates[108]. The technique of this reaction is simple and convenient, and it has therefore been applied in industry. The phosphorylation of cellulose is usually accomplished by heating the reaction mixture at 130–200° for from 15 min to several hours. In order to obtain a more homogeneous product and increase the reactivity of the cellulose, it has been proposed to subject the initial compound to preliminary scouring, desizing, and mercerisation[6].

In spite of the extensive literature on this method of phosphorylation, the effectiveness of the reaction has been obscure until quite recently. Many authors do not indicate the phosphorus content of their products, and sometimes publish extremely contradictory results. Thus the synthesis of a cellulose phosphate containing 11–13% of phosphorus has been reported[33], whereas similar work[101,103] has given specimens containing only 4–6% of phosphorus. The most careful investigation[102] has shown that a phosphorus content of 9% can be obtained only by repeating the phosphorylation procedure three times.

The structure of the cellulose phosphates obtained has not yet been finally elucidated. Most authors suggest that phosphorylation involves mainly the primary hydroxyls of the glucose units[3,120], but this has not been proved. Some research workers[6,26,31,120] regard the products obtained as primary and secondary phosphoric esters, pointing out that monoalkyl phosphates are formed on heating to 150°, and dialkyl phosphates above 150°.

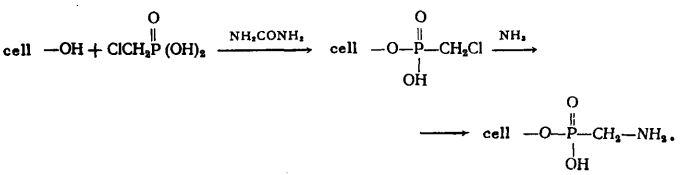
The secondary esters can be of two types — cyclic (I), in which the phosphorus atom is linked by the two bonds with only one glucose unit, and cross-linked (II).



(I) (II)

Several authors associate the formation of structures (I) or (II) with the appearance of definite properties in the resulting compounds, e.g. the cross-linking of the macromolecules through phosphorus with the acquirement of rotproof properties[98].

Alkyl phosphates[124,125] and *NNN'N'*-tetramethylphosphorodiamidic[81], chloromethylphosphonic, and hydroxymethylphosphonic[123] acids[42,43], besides phosphoric acid, can react with cellulose in the presence of nitrogen bases. Above 130° this reaction is accompanied by secondary ammonolysis of the chloromethylphosphonate, with formation of the cellulose aminomethylphosphonate[43]:



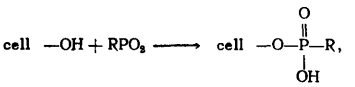
Phosphorylated celluloses obtained by the above method often possess poor mechanical properties, and are therefore unsatisfactory to the consumer. Recently, in order

to obtain less degraded products, phosphorylation has frequently been achieved with poly(vinyl phosphate)[28,30,40,103,124,125]. The loss in mechanical strength of the specimens thus obtained corresponds to the loss for cellulose phosphates containing one-third to one-quarter of the phosphorus content[103]. The mechanism of the reaction has not yet been elucidated; it is suggested that, depending on the conditions, either trans-esterification of poly(vinyl phosphate) by the cellulose or condensation with formation of a mixed phosphate of the two macromolecular compounds can occur[28].

Towards the end of the 1940s reports had appeared in the literature of the phosphorylation of cellulose with pentaerythritolphosphoric acids[126-133]. Reaction is usually complete at 130–180° in 15 min. The phosphorus content of the resulting phosphates does not exceed 3%. No comparison has yet been made of the characteristics of phosphorylated celluloses obtained in this way and by other methods. Nor are data available on the mechanism of this reaction.

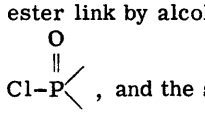
3. Phosphorylation by Other Reagents

Anhydrides of phosphoric acids are interesting phosphorylating agents for cellulose. The use of phosphorus pentoxide for this purpose has been patented[134,135]. Derivatives of meta-, pyro-, and poly-phosphoric acids have also found application[104,108,109,114,118,119,136]. It has recently been proposed to obtain acid phosphonates of cellulose by phosphorylating the latter with phosphonic anhydrides[137]:

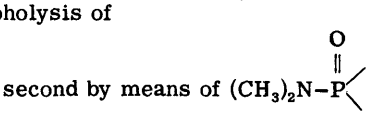


where R = CH_3, C_2H_5.

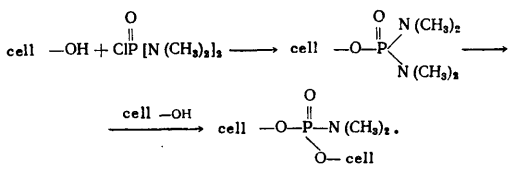
The phosphorylation of cellulose with amides and hydrazides of phosphorus is of definite value, e.g. with the corresponding polyphosphonitrilic derivatives[81,138,139]. In spite of the relatively high temperature (~ 140°) the reaction involves hardly any degradation of the polysaccharide, since no deleterious substances are evolved in the process. A reaction which develops by a mixed mechanism must also be mentioned. Thus tetramethylphosphorodiamidic chloride, on interaction with cellulose, forms its first ester link by alcoholysis of



, and the second by means of

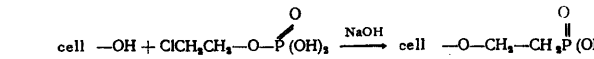


:[81]

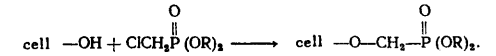


4. Indirect Phosphorylation

It appears that derivatives of cellulose containing phosphorus have been prepared in which hydrogen atoms of hydroxy-groups of the cellulose have not been replaced by acid radicals containing phosphorus. Treatment of cellulose with 2-chloroethyl phosphates in alkaline medium yields 2-phosphatoethylcellulose containing 1.3% of phosphorus[140]:

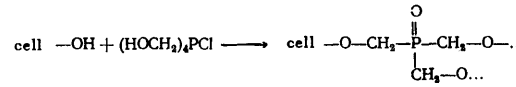


The phosphonomethylation of cellulose by the action of salts[22,25,40,45,141,142] or esters[45] of chloromethylphosphonic acid has been comparatively well studied:

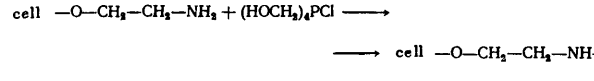


The phosphorus content of the resulting samples usually varies between 0.7% and 2%. The mechanical qualities of phosphonomethylcellulose are not very high, and it is therefore recommended that the initial material should first be treated with 1,3-dichloropropane for the partial cross-linking of the macromolecules[142].

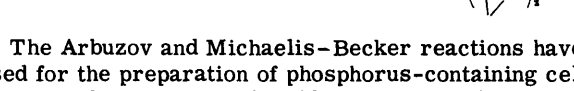
A phosphinylmethylated cellulose is formed when the polysaccharide is treated with tetrakishydroxymethylphosphonium chloride[23,24,143]:



It appears that aminoethylcellulose can be used in this reaction[144]:



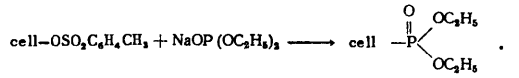
2-Phosphinylaminoethylcellulose has been obtained by the use of azirides of phosphoric or phosphorothioic acids as modifying reagents[145-147]:



The Arbuzov and Michaelis–Becker reactions have been used for the preparation of phosphorus-containing celluloses. Thus reaction of a chloroacetate with triethyl phosphite yields a product which was regarded as a phosphonoacetate[148]. In view of the results of a more detailed study of the Arbuzov reaction using α-halogeno-carbonyl compounds[149], such a structure cannot be entirely justified for the product obtained. Quite recently a study has been made of the reaction of chlorodeoxycellulose with triethyl phosphite[77]:

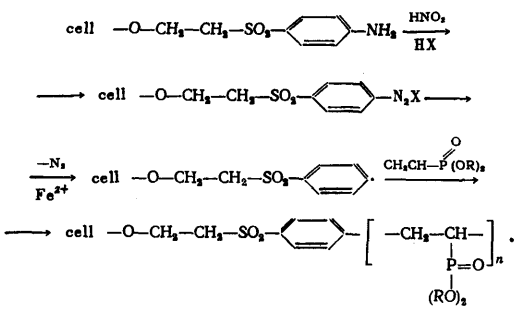


The product contains 5% of phosphorus. An analogous material is obtained by the interaction of cellulose toluene-*p*-sulphonate with sodium diethyl phosphite[13]:



Recently an original method has been developed in the Soviet Union for preparing phosphorus-containing cellulose derivatives by grafting vinylphosphonic esters to the cellulose. The principle of the method consists in introducing a small quantity of aromatic amino-groups into the macromolecule. After diazotisation of the amino-derivative in

the presence of a reducing agent, e.g. a ferrous salt, nitrogen is evolved and macroradicals are formed, which initiate the formation of graft chains on the cellulose. The 2-sulphanilylethyl ether has been used as cellulose derivative containing an aromatic amino-group [150]:



The phosphorus content of the product does not usually exceed 4–4.2%.

III. PHOSPHITYLATION OF CELLULOSE BY DERIVATIVES OF ACIDS OF TERVALENT PHOSPHORUS

During recent years interest has grown in macromolecular compounds containing acid radicals of tervalent phosphorus. There are obviously three main reasons for this: firstly phosphitylation with acid derivatives of tervalent phosphorus is usually more efficient and occurs under milder conditions than with derivatives of quinquevalent phosphorus [64]; secondly, macromolecular phosphites and phosphonites can be readily converted by reactions of polymeric type into various derivatives of acids of quinquevalent phosphorus which it is difficult or even impossible to obtain by direct phosphorylation [151]; and thirdly, macromolecular derivatives of tervalent phosphorus acids possess specific properties which make them promising for industrial exploitation, e.g. as antioxidants and stabilisers for polymers [152,153], additives in oils [154], etc.

All this obviously applies to modified celluloses containing acid radicals of tervalent phosphorus. Since 1960, therefore, patents and scientific publications have started to appear systematically on the preparation and properties of these compounds.

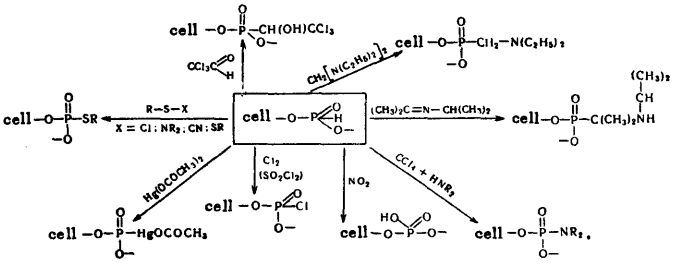
1. Phosphitylation by Acid Chlorides

Only one report has appeared on this topic, acetates, butyrates, and other esters of cellulose being phosphitylated with alkyl(or aryl)phosphonous dichlorides and dialkyl(or diaryl)phosphinous chlorides in the presence of tertiary amines [73]. In view of the complexity of the phosphitylation of cellulose with chlorophosphines and similar compounds, as well as the publication of a large number of papers on new methods for the mild phosphitylation of hydroxy-compounds with other reagents, little development on these lines is to be expected in the future.

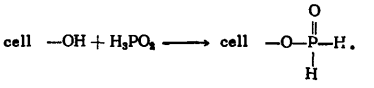
2. Phosphitylation by Acids

Phosphorous acid is known to be an effective phosphitylating agent [155], and its reaction with cellulose has therefore been studied. The reaction can be accomplished in several ways — by phosphitylation in an organic solvent, in molten phosphorous acid, or in an inert gas [156] — the second method enabling cellulose phosphites to be obtained containing up to 17% of phosphorus, though the product is strongly degraded. It is most convenient to modify cellulose by the third method [156], the optimum temperature being 120–130°, the duration being 3–15 h, and the phosphorus content reaching 14%.

The products obtained, which are acid phosphites, are reactive compounds which can be converted by reactions of polymeric type into cellulose derivatives containing fragments of various acids of quinquevalent phosphorus [157]:



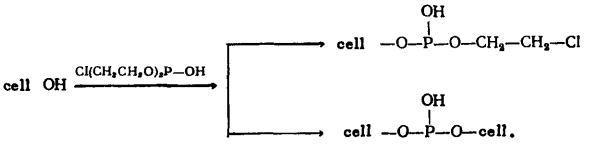
Quite recently cellulose has been phosphinylated by heating it with hypo-phosphorous (phosphinous) acid [158]:



In view of the high coordination and saturation of phosphorus in the compounds obtained, they show great promise for various chemical transformations.

3. Phosphitylation by Esters

As efficient phosphitylating agents, esters of tervalent acids of phosphorus are employed also for the phosphitylation of cellulose. A comparatively detailed study of this reaction has been made on mono- [157,159], di- [160–162], and tri-alkyl (or -aryl) phosphites [162,163] of various types and on acid phosphonites [160,164]. Transesterification of acid phosphonites with the reaction products gives cellulose phosphonites cell–O–P(CH$_3$)–OH in which γ = 150. The transesterification of di- and tri-alkyl (or -aryl) phosphites is a more complex process, products being formed in which one, two, or three alkoxyls (or aroxyls) have been replaced by a polysaccharide residue. The reaction can be followed by introducing a phosphite in which the alkyl radical contains a halogen atom. In the transesterification of bis-2-chloroethyl phosphite, for example, the content of phosphorus and of chlorine in the reaction product is used to establish under what conditions polyesters containing mainly alkyl glycosyl phosphite or mainly diglycosyl phosphite fragments are formed [162]:

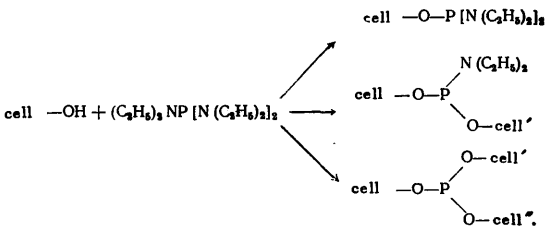


Acid phosphites of the cellulose series, especially those obtained with industrial dimethyl phosphite [161], are of

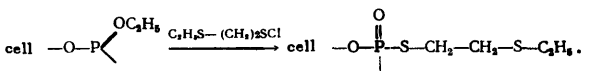
interest for the preparation of various phosphorylated celluloses. They have been converted into compounds containing fragments capable of complex formation, pesticidal activity, etc.[161]

4. Phosphitylation by Nitrogen-Containing Derivatives

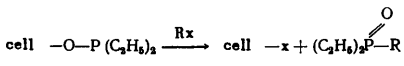
One of the most effective and convenient methods of phosphitylation is the alcoholysis of amides of tervalent acids of phosphorus[165]. This reaction has been applied also to cellulose[166]. Tetraethylphosphinous amide, ethyl tetraethylphosphorodiamidite, and phosphorus hexaethyltriamide have been studied as phosphorylating agents. In the first case a cellulose diethylphosphinite is formed (under optimum conditions the degree of phosphorylation is close to 20%); in the second and third cases, amido-esters or cross-linked esters of cellulose are obtained, e.g.



The normal phosphites and the phosphinites of cellulose which have been prepared are reactive compounds, being oxidised to the corresponding quinquevalent derivatives merely by the action of oxygen[166]. With sulphur they give phosphorothionates and phosphinothionates not hitherto described in the literature. With sulphenyl chlorides, cellulose phosphates are converted into phosphorothiolates. In this way it has been possible to prepare a phosphorylated cellulose containing residues of the well-known insecticide Isosystox[166]:



Dialkylphosphinites of cellulose, like simple esters of tervalent phosphorus, undergo the Arbuzov reaction, forming a deoxyhalogenocellulose:



A paper has appeared very recently on the phosphitylation of cellulose with hydrazides of phosphorous acid. Thus 1-methyltrimethylene dimethylphosphorohydrazidite acylates cellulose under milder conditions than in the corresponding preparation with amides[167].

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A large amount of research has been done on the phosphorylation of cellulose, but a certain uniformity of chemical approach to phosphorylation can be seen in most of the work. In recent years success has been achieved in developing new ways of phosphorylating cellulose by methods which have not yet become "classical". These investigations may be expected to yield new phosphorus-containing materials of interest for the national economy.

Fresh progress in the phosphorylation of cellulose will depend to a considerable extent on the attention paid to physicochemical laws in conducting these transformations of polymeric type.

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Chemical Faculty,
Lomonosov Moscow State University

U. D. C. 541.61

OXIDATION–REDUCTION POLYMERS

E. E. Ergozhin and F. T. Shostak

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1. INTRODUCTION†

Great interest has arisen in recent years in macromolecular compounds of a new type, oxidation–reduction polymers or, as they are still called, electron exchangers. The latter term has been coined by analogy with ion exchangers, but its choice is unfortunate, since the oxidation or reduction of a polymer does not involve the

† Fresh results have been published since this paper was submitted for publication, and are collected together in the supplementary references[205-275].