

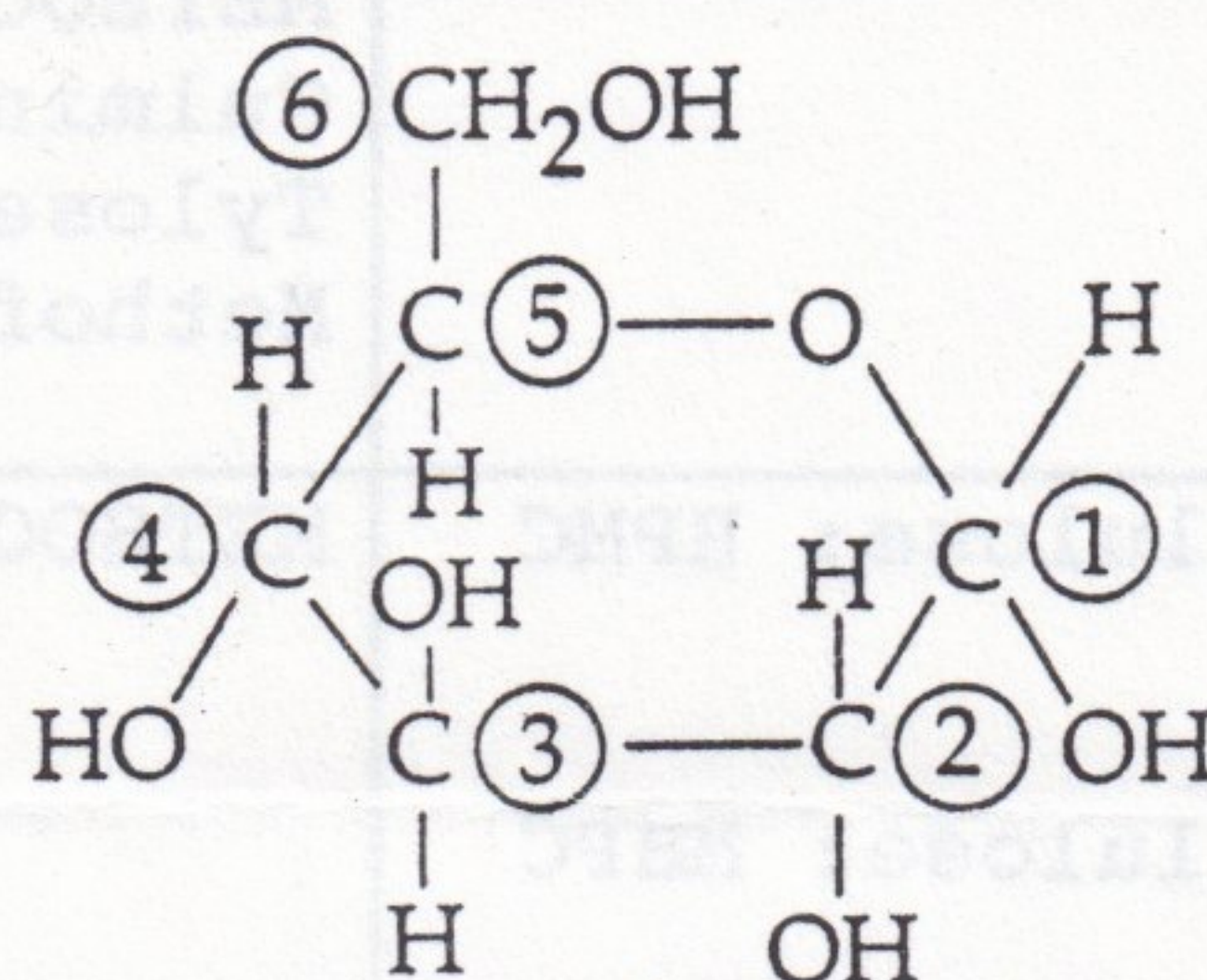
Cellulose Ethers: Practical Considerations for Use in Conservation

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Over the last twenty years, cellulose ethers have become an indispensable tool to the conservator. In the past, they have been used more often in the conservation treatment of cellulose-based artifacts such as paper and textiles, but they are becoming increasingly common in paintings and object conservation. One of the reasons for their popularity lies in the many ways they can be used: as poultice materials; as consolidants and fixatives; as sizing agents; as adhesives; as surfactants; as cleansing agents; as deflocculants and flocculants; as extenders for use with other adhesives; as binders for pigments to make retouching media; etc. The many ways that cellulose ethers can solve treatment problems seem to be limited only by the imagination of the conservator.

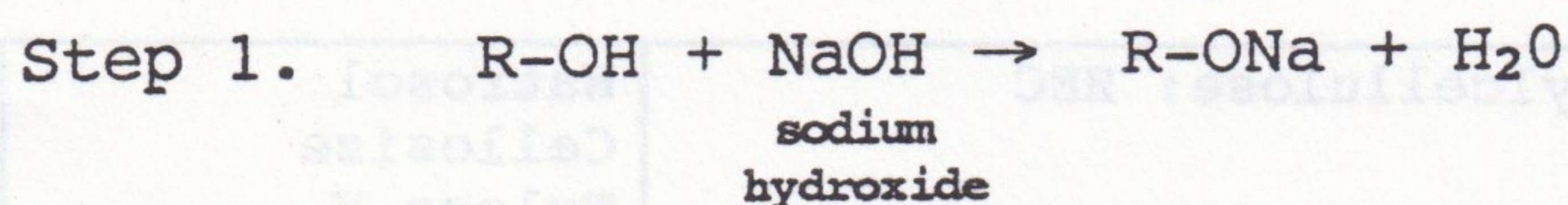
To help acquaint the conservator with the chemical and physical properties of these materials, the following information is presented as background. All cellulose ethers have in common a C-O-C (carbon-oxygen-carbon) bond which is created when an organic material undergoes the etherification procedure. Cellulose ethers are made by first treating cellulose from either cotton linters or from chemical wood-pulp with a strong alkali, usually sodium hydroxide. The alkali cellulose is then chemically altered with one or more of a variety of compounds in the substitution process known as etherification. Specifically the ether group is substituted for the H⁺ in the OH⁻ group on the carbons numbered 2, 3, and 6 - see the cellulose unit.



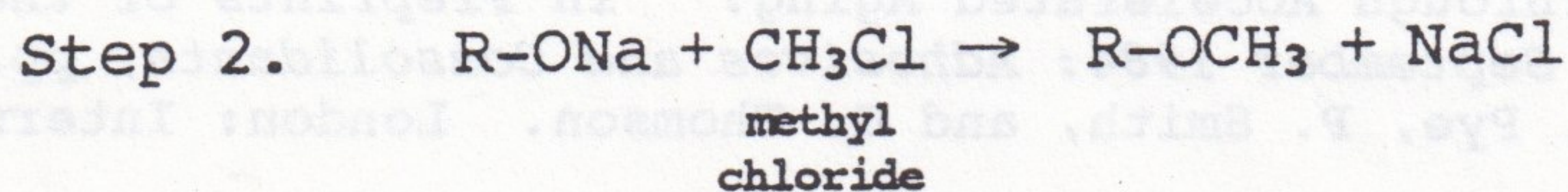
cellulose unit

Many of the characteristics of a cellulose ether, e.g. solvent, are dependent not only on the ether group, but also the degree of substitution (DS) onto the cellulose unit. In the etherification of cellulose, the theoretical DS maximum would be 3.0, but in practice this maximum is not possible to achieve. In fact, because it is very difficult for the DS to be exactly planned or determined, a range of DS values for cellulose ethers is usually given by the manufacturer. Since the DS values could vary considerably from batch to batch, the conservator should be aware that cellulose ethers purchased in different batches may have different properties.

For example, methylcellulose is made by first treating native cellulose with a strong alkali such as sodium hydroxide, NaOH. This reaction is illustrated in Step 1.



The alkalized cellulose then undergoes etherification by treating it with methyl chloride, CH₃Cl as in Step 2.



The DS values of methylcelluloses used commonly in conservation are between 1.3 - 2.0. In some of the cellulose ethers, such as hydroxypropylmethylcellulose, both hydroxypropyl groups and methyl groups can be substituted onto the alkalinized cellulose unit.

Another term encountered when speaking of polymers, is the degree of polymerization (DP), which is an indication of chain length. Generally, the higher the DP number, the longer the polymer chain, and the higher the viscosity of the methylcellulose. The viscosity of any cellulose ether is controlled by altering the DP of the native cellulose before etherification.

Also, it is generally true that the higher the DP of a polymer, the more stable it is to aging, and perhaps the one primary concern we have about any conservation material is its stability. There have been a few articles published, including one by me in 1984 for the IIC Paris Conference on Adhesives and Consolidants¹, which seem to indicate that at least some cellulose ethers are stable when artificial aging is used to compare them to similar materials such as starch paste, gelatin, PVA, etc.

In 1990, the Getty Conservation Institute published an important book by Feller and Wilt, entitled *Evaluation of Cellulose Ethers for Conservation*.² I would recommend it to all of you who want to get background information on these useful materials. Here is my summary of Feller and Wilt's findings with regard to the stability of the cellulose ethers they tested.

GROUP (Rank)	GENERIC NAME: ABBREVIATION	BRAND NAMES	MANUFACTURER (FORMER)
A (1)	Methylcellulose: MC	METHOCEL A Culminal Tylose MB Methofas M	Dow Aqualon (Henkel) Hoechst ICI
A (2)	Hydroxypropylmethylcellulose: HPMC also known as: Methylhydroxypropylcellulose: MHPC	METHOCEL E, F, J, K	Dow
A (3)	Sodium carboxymethylcellulose: SCMC	Cellulose Gum Cellofas B Tylose C	Aqualon (Hercules) ICI Hoechst

B	Ethylhydroxyethylcellulose: EHEC-WS (WS=H ₂ O soluble) Note: with more testing, EHEC-WS may move to Group A, Feller/Wilt.	Modocoll E Ethulose 400	Mo och Domsjo Mo och Domsjo
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C (1)	Hydroxyethylcellulose: HEC	Natrosol Cellosize Tylose H	Aqualon (Hercules) Union Carbide Hoechst
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¹ Baker, C. "Methylcellulose and Sodium Carboxymethylcellulose: An Evaluation for Use in Paper Conservation Through Accelerated Aging." In *Preprints of the Contributions to the Paris Congress, 2-8 September 1984: Adhesives and Consolidants*, pp. 55-59. Edited by N.S. Brommelle, E.M. Pye, P. Smith, and G. Thomson. London: International Institute for Conservation, 1984.

² Feller, R. L. and Wilt, M. *Evaluation of Cellulose Ethers for Conservation*. Marina del Rey, CA: Getty Conservation Institute, 1990, pp. 93-96.

C (2)	Hydroxypropylcellulose: HPC	Klucel	Aqualon (Hercules)
C (3)	Ethylhydroxyethylcellulose: EHEC-OS (OS=org. solvent soluble)	EHEC-OS	Aqualon (Hercules)
C (4)	Ethylcellulose: EC	ETHOCEL Ethylcellulose	Dow Hercules

GROUP A includes those cellulose ethers which can be regarded as 1st class materials, and within each group, specific cellulose ethers are ranked 1,2,3 etc. All of these cellulose ethers exhibit excellent to very good stability, and therefore, they can remain in, on or near the artifact after treatment. The conservator should feel quite confident in their permanence. All of these cellulose ethers are initially soluble only in water.

GROUP B can be regarded as intermediate materials. Only one cellulose ether, currently, falls in this category. Feller and Wilt placed the water soluble EHEC in this group because they felt that it had not been tested enough. They did predict, however, that with further testing, it could prove to be a Group A material.

GROUP C materials can be regarded as generally unstable, and therefore, should be used with caution as "temporary" conservation materials. In other words, if at all possible, they should be entirely removed from the artifact before the treatment is completed. Many of these cellulose ethers have been used in conservation treatments because they are soluble in organic solvents. When the artifact under treatment is sensitive to water, this can be a distinct advantage.

To summarize this chart, then, when treating porous materials such as paper and textiles, the conservator should use GROUP A cellulose ethers whenever possible. Caution should be used when considering Group C materials.

Now all the conservator has to do is figure out how to use these materials in the best possible ways. Although many conservators seem to think methylcellulose and sodium carboxymethylcellulose are very similar, one can see real differences between them. In some conservation treatment steps, methylcellulose might be the best one to use; in others, sodium CMC. For example, not all cellulose ethers are good adhesives, not even the ones within GROUP A.

Methylcellulose	Sodium carboxymethylcellulose
nonionic	ionic
poor bonding strength	good bonding strength
powder/film increasingly soluble <80°C; not soluble >80°C	powder/film soluble in cold-hot water
high surface activity "wet"	low surface activity "dry"

Taking these properties into account, the conservator can tailor one or a succession of water-soluble cellulose ethers to do the job at hand. Going hand-in-hand

with the above properties are viscosity grades and the affect of concentration of solutions. If conservators are to use these and similar materials in the most efficient way, these properties must also be well understood. The term "viscosity grade" is used to define the viscosity of different methylcelluloses, and it is determined by measuring each methylcellulose under the same conditions of concentration, solvent, and temperature.

Viscosity can be measured in a number of ways and is often expressed in centipoise (cP).

METHOCEL A

(methylcellulose, manu. by Dow Chemical Co.)

Viscosity Grade	Average Centipoises
4M	4000 cPs
15C	1500 cPs
4C	400 cPs
15	15 cPs

Note: all measured at 2% in water at 20°C.

For example, Dow Chemical Co. - the manufacturer of the methylcellulose METHOCEL A - states that the viscosity of METHOCEL A 4M, measured in a 2% solution of water at 20°C, is between 3000-5000 cPs. The methylcellulose is labeled 4M to designate an average of 4000 cPs. Three other viscosity grades of METHOCEL A are 15C or 1500 cPs; 4C or 400 cPs; and 15 or 15 cPs. Because viscosity is linked to DP, METHOCEL A 4M forms long chains of methylcellulose in solution while METHOCEL A 15 forms very short chains.

The high viscosity grades of cellulose ethers, for example METHOCEL A 4M, form long chains which become increasingly entangled with each other with higher concentrations. When applied to paper, the polymer is so tangled that it might not be able to penetrate far into the paper. However, the water is absorbed into the paper. This gives the conservator the impression that the entire solution is being absorbed. When the paper is dry, the polymer film might form on the surface to which it was applied. This film often produces a glossy or sparkling effect on the paper's surface. If penetration of a high viscosity grade cellulose ether is required, then the concentration to be used must be low enough so that this film formation is avoided. The problem is that since the concentration might be about 1%, there would be so little polymer in the paper that its properties which are to be imparted to the artifact might be insufficient. (Note: Even if the right cellulose ether is chosen and used in the correct concentration, a film may still form on the surface after treatment. This is due to the fact that upon evaporation of the water, the polymer will be carried up to the drying surface to be deposited there as a film. To avoid this, dry the treated paper in a microenvironment (in a press, or between drying screens) so that evaporation occurs over a longer period of time and occurs evenly across both surfaces. If dried in this way, the cellulose ether will tend to remain in the paper.)

Lower viscosity cellulose ethers, for example METHOCEL A 4C, because they are composed of much shorter chains, are able to be used in much higher concentrations because they tend not to intertwine with one another. Therefore in the same high concentrations, the lower viscosity METHOCEL A 4C will be able to penetrate more effectively into the paper compared to METHOCEL A 4M.

Therefore for conservation applications requiring increasingly greater penetration - such as resizing and consolidation, the medium or medium low viscosity grades of methylcellulose in high concentrations should be used.

It is also possible to sequentially apply methylcelluloses with different viscosity grades. For example, if METHOCEL A 4C in a high concentration is applied to paper, it

will penetrate into the paper. A paper so internally sized could be expected to tolerate the effects of rapid fluctuations of relative humidity, to resist liquid penetration, and also to provide increased internal strength. However, the surface of that internally sized paper might not be adequately protected against air-borne pollutants or acids and oils from handling. As methylcellulose provides a very good barrier to oils and grease, it would protect papers which are to receive a lot of handling. A surface size of methylcellulose might be used in addition to the internal size or it could be used alone. In this case, a high concentration of METHOCEL A 15C or 4M might be used. The methylcellulose could be applied to one side of the paper, air dried, and then applied to the other side.

Mixtures of medium and medium low viscosity grades, for example, 15C and 4C, might be used to internally and externally size the paper. If using mixtures in this way, it is important to use a solution concentration which would allow the shorter chain polymer to penetrate into the paper while the longer chained methylcelluloses, being unable to disentangle, to form films on the surfaces. Again, the best way to achieve this would be to brush-apply the mixtures to first one side, allow to dry, and then similarly treat the other side.

Decisions about which viscosity grade and proper concentration to use for either internal or surface treatments should be carefully considered. A significant film of methylcellulose on the surfaces of papers and textiles, especially those which would be stored in direct contact with similarly treated surfaces, might lead to problems with "blocking" or sticking together. This problem would be more evident in environments where high relative humidity levels are a problem.

Although low viscosity grade methylcelluloses such as METHOCEL A 15 would penetrate paper very well, they have not been tested to determine their long-term stability. One might predict that, because the chains are so short, the degradation of this methylcellulose might occur at a greater rate than has been seen in the higher viscosity grade methylcelluloses.

For conservation applications requiring little penetration of the paper - such as for adhesives, poultices, and surface cleansers - a high viscosity grade of methylcellulose in high concentrations should be used. An example of a very good, all purpose adhesive mixture, which has been used in the Art Conservation Department over the past six years, is composed of 1 volume of 25% wheat starch paste to 2 volumes of 2.5% METHOCEL A 4M. Blend, sieve or knead the paste to a smooth consistency before carefully folding in the methylcellulose. This adhesive mixture derives strength from the paste while flexibility and easier reversibility come from the methylcellulose. Another advantage is that this mixture remains "fresh" if stored in a closed container in the refrigerator for long periods with no need to use any fungicides.

In conclusion, cellulose ethers have become indispensable materials used in many conservation labs over the past twenty years. However, in many labs only one or two cellulose ethers are used to solve many different problems. Differences in the properties of cellulose ethers account for inconsistent results noted by conservators - for example, one conservator might praise methylcellulose for a certain application, while another condemns it. As with any material, purchasing a cellulose ether from a conservation supplier without knowing the following essential information might lead to disappointing and inexplicable results.

Conservators should expect suppliers to publish, or at least make available upon request, information about the brand name, manufacturer, purity, viscosity, and date of manufacture of any cellulose ether. With regard to purity, pharmaceutical grade is strongly recommended, food grade is acceptable if pharmaceutical grade is not available, but industrial or technical grade is not recommended. Optional information would include the degree of substitution and the degree of polymerization, and this information would be available from the manufacturer.

Write to the manufacturer and ask for the technical information, the MSDS, instructions for making solutions, and a sample of the various types and grades available. Experiment with the different grades and concentrations to see for yourself how different these materials can be, and how they might be useful to you.

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