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CHARACTERIZATION OF CELLOPHANE AS
AN IONIC BARRIER

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11 MARCH 1964

NOL

UNITED STATES NAVAL ORDNANCE LABORATORY, WHITE OAK, MARYLAND

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CHARACTERIZATION OF CELLOPHANE AS AN IONIC BARRIER

Prepared by:
Claudia C. Evans

ABSTRACT: Cellophane, a gel developed from crystalline alpha-cellulose, has been used as an ionic barrier (battery separator) in electric batteries with outstanding success for many years. Understanding the mechanism of the cellophane action in ionic barrier applications could lead to the development of superior ionic barriers.

A literature survey has been conducted on the characteristics of cellophane as related to electrochemical cell barrier applications. The physical or chemical bonding of ions in electrolyte solutions to molecules in the membrane, or the catalytic complexing of undesirable ions appear to be much more important in the effective operation of cellophane as a barrier than the filtering or capillary diffusion actions, although these latter actions cannot be ignored.

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U. S. NAVAL ORDNANCE LABORATORY
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This literature survey on cellophane has been conducted as part of a Battery Evaluation and Supporting Research project supported by RUTO 3E000/212. This project is directed toward understanding and improving the performance of the silver-zinc battery. A study of the ionic species involved in the battery reactions has been under way for some time. It is apparent that the ionic barrier (separator) used in this system is extremely critical to the successful construction of a battery. In preparation for a program expansion into a separator study, the readily available literature has been reviewed. This bibliography of pertinent literature on cellophane as an ionic barrier is proffered as a starting point for a more advanced or specialized separator study.

R. E. ODENING
Captain, USN
Commander

Alfred Lightbody
A. LIGHTBODY
By direction

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INTRODUCTION

1. Knowledge of the mechanism contributing to the outstanding performance of cellophane in the zinc, potassium hydroxide, silver oxide electrochemical cell is considered fundamental to the continued improvement of this system. Such information could probably be applied to other electrochemical systems requiring the separation of ionic species for satisfactory performance. Since this Laboratory has not been actively engaged in "battery separator" studies, a literature survey for background information was conducted during the summer of 1963 in two allied fields: a general survey of mechanisms of ionic solution conduction through membranes, and a specific study of the properties of cellophane as an ionic barrier and ionic conductor. This is a report of the findings in the latter study.

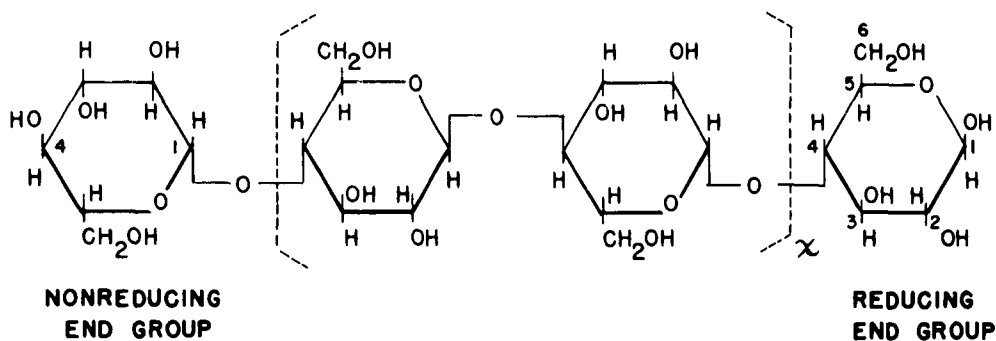
2. In the silver oxide-zinc battery system the basic requirements of a good separator are "low resistance, good chemical stability in the alkaline, oxidizing environment, a pore structure capable of restricting the migration of soluble or colloidal silver, and minimum membrane thickness."² Cellophane has been a successful and widely used separator material. As a separator it has "achieved the following objectives: (1) immobilization of the electrolyte by absorption in the cellulose, (2) elimination of the gases evolved in the operation of the cell, (3) prevention of mutual penetration of the active materials, and (4) homogeneous and reversible deposition of the negative active material (Zn) from the electrolyte."²⁹ Unfortunately, cellophane does suffer from instability in an alkaline oxidizing battery environment in which zinc trees may even build up and puncture it, causing a short circuit between the electrodes. However, since cellophane is for the most part a successful and widely used battery material, the separator study might be aided by a further knowledge and understanding of what exactly cellophane is and of the structure and properties that make it a suitable separator.

3. One of the requirements of the separator in the silver oxide-zinc battery is to stop the diffusion of silver either by acting as a selective barrier or by selectively absorbing and preventing its passage through the separator membrane. Thus, an understanding of the reaction of silver with cellophane, of the migration or transport mechanism of the silver, and of the structure of the cellophane might aid the study of the mechanism of separation. It might also lead to some ideas or suggestions concerning the ideal separator which would resist the passage of zincate and soluble silver ions and not be attacked by KOH.

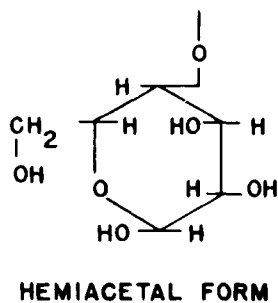
4. Because of a difficulty in finding information on the reactions and structure of cellophane, considerable attention was focused on cellulose.

PHYSICAL AND CHEMICAL STRUCTURE OF CELLULOSE

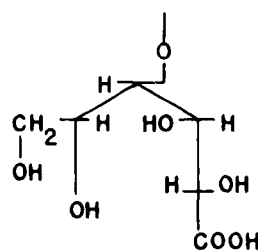
5. Cellophane is cellulose [empirical formula $(C_6H_{10}O_5)_n$] which has been regenerated by oxidation and degradation. X-ray diffraction studies⁶ reveal that the cellulose molecule consists of a long chain of β -glucose anhydride units linked together by primary valences through oxygen bridges at the 1- and 4-positions (β -glucosidic ether linkages), each unit containing three free hydroxyl groups in positions 2, 3, and 6.



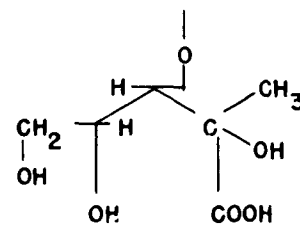
The end groups may be of the following form:⁵



1



2



3

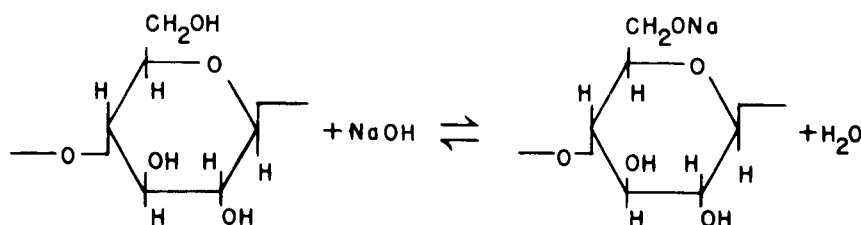
6. Cellulose consists of chains of glucose residues which have covalent bonds occurring at intervals of 25 - 30 glucose units which unite the chains laterally yielding a 3-D type arrangement. These secondary valence forces which hold the chains alongside in bundles may be of the van der Waals type and be due to the polar groups in the chain [hydroxyl or aldehyde (oxygen bridge) groups].

7. Forty to sixty chains in a bundle form a micelle or crystallite which has an average width of around $50 \text{ \AA}$ and length of around $500 \text{ \AA}$. Since the parameters (7.9 , 8.35 , and $10.3 \text{ \AA}$) of the unit cellulose crystal cell (monoclinic) do not change when cellulose undergoes swelling, this indicates that the water and ions must penetrate between the individual crystallites where the tertiary valence forces are weaker. Regenerated cellulose fibers show the mercerized crystalline structure in which the inner micellar surface has doubled making intramolecular hydroxyl groups more accessible to liquids. Cellulose has a micelle structure in which there is a continuous transition between the chains which have crystallized and the non-crystalline or amorphous regions. Attack on the amorphous uncrystallized portions of the cellulosic fiber results in degradation in which portions of the fiber fall into a powder while the crystallized portions are left less severely damaged.

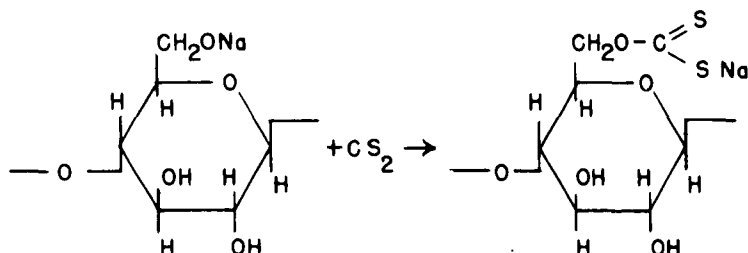
8. Reactions with cellulose may take place by either of two ways: (1) rupturing the linkages of the chain holding the units together (reaction as a polysaccharide in which oxidation causes cleavage of glycosidic linkages and results in shorter chains), and (2) reacting with the hydroxyl groups (reaction as a polytrihydric alcohol containing two secondary and one primary hydroxyl groups per unit of glucose in which oxidation of hydroxyl groups results in aldehyde and carboxyl groups).

MANUFACTURE OF CELLOPHANE

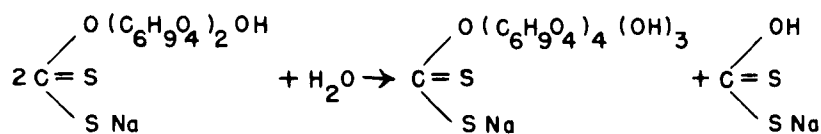
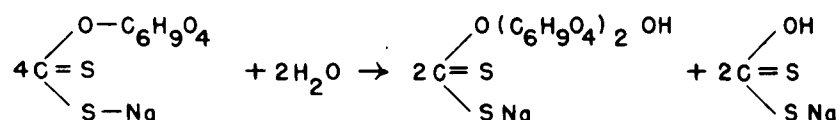
9. Sulfite wood pulp of high alpha-cellulose content is steeped in sodium hydroxide solution to produce sodium or alkali cellulose.



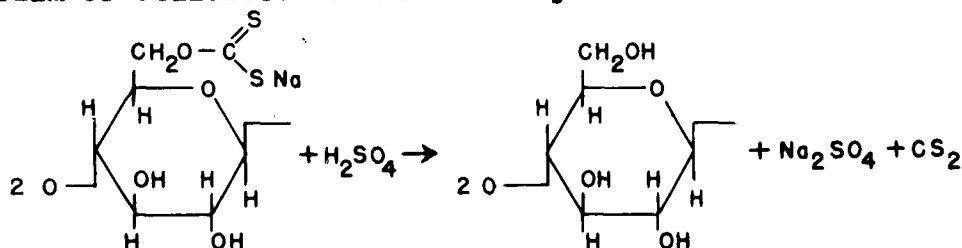
After aging the alkali cellulose is treated with carbon disulfide to form the ester cellulose xanthogenate (sodium cellulose xanthate).



10. A colloidal suspension forms when cellulose xanthate is mixed with dilute sodium hydroxide. The viscose undergoes a series of reactions during a "ripening" period in which there is a partial hydrolysis of the xanthogenate with the formation of sodium thiocarbonate as the molecule becomes more complex.²¹



11. In the coagulation bath, after extrusion the viscous film of cellulose xanthate is regenerated into cellulose film.



In the regeneration process there is "first, the coagulation or salting out of the viscose and neutralization of the alkali present by the sulfuric acid in the bath; and secondly, the decomposition of the precipitated cellulose xanthogenate to hydrate cellulose."²²

PHYSICAL PROPERTIES OF CELLOPHANE

12. The thickness range of commercial cellophane is from 0.0009 to 0.0017 inch. It has high resistance to initial tear but relatively lower resistance once the tear has started. Its tensile strength is 10,000 psi. Because of a somewhat random orientation of micelles in cellophane the mechanical strength is reduced when the hydroxyl groups which hold the chains alongside become saturated. In order to define the physical properties of cellophane it is necessary to designate the values in both the longitudinal and transverse direction. For instance, the tensile strength is greater in the longitudinal direction, which is the direction of the film's forward movement through the casting machine, whereas the elongation is greater in the transverse direction. Tenacity and elasticity and their directions depend on the amount of crystalline material and on the orientation or degree of randomness of the micelles.

13. Cellophane is transparent to both ordinary and ultraviolet light. It is assumed that the ultraviolet light waves may rupture the cross linkages at a faster rate than the normal glycosidic linkages. Cellophane appears to have two optical axes. It exhibits the anisotropic properties of cellulose²¹ and has polarizing properties. Cellophane has excellent dielectric properties, especially at higher temperatures when the restraining forces between neighboring parallel chains have lost effect allowing the glucose units freedom to rotate about their oxygen bond (-O-) under an applied field.⁵³

14. Cellophane per se is not porous. Its capillaries are believed to be of the transient type that exist due to the presence of a swelling agent. Its numerous hydroxyl groups allow cellophane to swell readily in an electrolytic solution. The capillary paths do not run straight through the material and they are not of a uniform pore radius. The size of the capillaries have been measured by a variety of methods including those using an osmometer and Poiseuille's equation, the void volume method, and the conductance method.²⁵ Values of pore radii such as 0.02 μ to 0.03 μ or 15 $\text{\AA}$ have been given. Cellophane is very permeable to water vapor and gases such as ammonia and carbon dioxide but relatively impermeable to hydrogen which is only slightly water soluble. It is readily permeable to electrolytes and other ionic species. In the

silver oxide zinc battery too much swelling and permeability would weaken the structure of the cellophane and would result in zinc deposits within its pores.

15. In the book Diffusion and Membrane Technology it is stated that "whereas alpha-cellulose is fundamentally crystalline, regenerated cellulose is fundamentally a gel which shares the properties of other gelatinous materials which are hydrophilic."⁵⁶ L. B. Ticknor attempted to resolve the theories of cellophane's being a gel or a porous mass.⁵⁵ From this study it was concluded that the permeation of cellophane involves both viscous and diffusive flow which indicates that the capillaries' radii are of molecular dimensions. Whether the predominating flow is viscous or diffusive will depend on the size of the capillaries, on the size of the molecules of the permeant, "and the bonding of the permeant to the film."⁵⁵ Much work was also done by a Canadian group on permeability by use of the void volume or conductance method.²⁵ "Many factors such as porosity of the membrane, temperature, pH, solvent, ionic strength; etc., were found to influence more or less the rate of diffusion of a particular solute through a membrane (and)... the relative rate of diffusion of one solute as compared to another."⁸ "The nature of the membrane includes its thickness, the amount of porous space, the size and shape of the pores, its adsorptive properties and its ion exchange properties."⁸

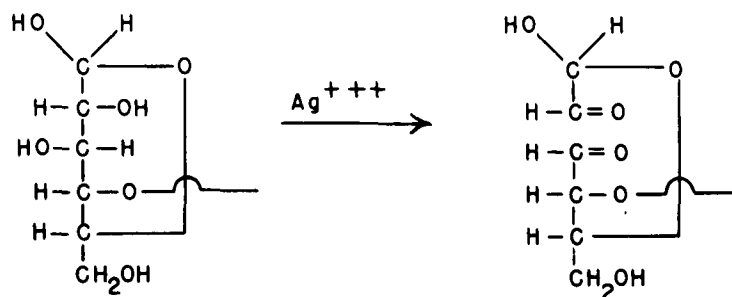
CHEMICAL PROPERTIES OF CELLOPHANE

16. Cellophane possesses a lower molecular weight and is more active chemically than natural unpurified cellulose. This indicates that the transformation to cellophane of high alpha content cellulose is both a chemical and structural change. "Not only is the molecular weight of the linear polymer greatly reduced but the orientation which reduces susceptibility to chemical attack as a consequence of steric hindrance is largely lost."⁵⁶ Cellophane is subject to attack from acids and even alkalies. "It undergoes the typical cellulose reactions, such as nitration, ethylation, xanthation, and swelling with caustic solutions."²¹ As with cellulose the speed of attack is probably determined by the degree of swelling and is probably directed to the amorphous uncrystallized portions of the fiber causing it to fall into a powder while the crystallized portions are left undamaged.

CELLOPHANE AND SILVER

17. Reactions with the cellulose molecule may occur with the hydroxyl groups or by disrupting the linkages of the cellulose chain. Since one of the requirements for the separator

in the silver zinc battery is to act as a selective barrier or to selectively absorb the silver and thus stop its diffusion through the membrane, a study of the reaction of silver with cellophane might be beneficial, for cellophane does hinder the migration of silver ions until it loads up. It is believed that the silver is reduced to its metallic form.⁴⁷ According to Patent No. 2,915,579, Mendelsohn in discussing the reaction of silver ions with cellophane states the following: "This reaction is believed to involve the rupture of the glucosidic linkages joining the glucose units of the polymeric cellulosic chain. As a result of this reaction, the sheet material is decomposed to a powder."³⁰ In a Brooklyn Polytechnic Institute report it states that in the reaction of trivalent silver ions with cellulose in a KOH solution, each of the cellulose's alcohol groups is oxidized to an aldehyde or acid while the silver ion is reduced to its metallic form as has been revealed by X-ray diffraction methods.¹⁵



18. The amount of decomposition of cellophane depends on the Ag content in the KOH solution. The solubility of silver oxide depends on the concentration of KOH or the number of hydroxyl ions present. An experimental study might involve the determination of the amount of metallic silver as a result of decomposition that is present in the KOH which might also account for the deposits on the cellophane.¹¹

19. According to Tuwiner in Diffusion and Membrane Technology, pure cellulose possesses ion exchange properties since by oxidation it is carboxylated. "The carboxyl possesses a weak attraction for alkali ions although other metal ions are held with some considerable stability, thus accounting for the ash content. If cellulose is de-ashed by electrodialysis, the absorption of silver ions is sometimes taken as a measure of carboxyl content."⁵⁶ In order to measure the complete amount of silver absorbed by the separator, according to the Brooklyn

Polytechnic report, it was necessary to ash the cellophane and dissolve the ash in dilute nitric acid in addition to just initially trying to remove from the cellophane the absorbed silver with nitric acid.¹⁵ This report discusses two methods, the catalytic method (p. 18) and the potentiometric titration method (p. 38), for the micro-determination of silver.

20. "Since a stoichiometric equation for the reaction between cellophane and silver cannot be written, a 'pseudo' formation constant (K_f) was calculated,"⁴ using the form $\text{RCOO}^- + \text{Ag}^+ \rightleftharpoons \text{RCOOAg}$, where the formation constant

$$K_f = \frac{(\text{RCOOAg})}{(\text{RCOO}^-)(\text{Ag}^+)}$$

$$= \frac{(\text{silver bound})}{\left(\frac{\text{total silver capacity}}{\text{minus silver bound}} \right) \left(\frac{\text{free silver}}{\text{external solution}} \right)}$$

21. The silver mirror test is based on the fact that aldehydes and α -hydroxyketones reduce complex silver ammonium salts. Glucose likewise exhibits a similar reducing action, although to a lesser extent since there are fewer carbonyl forms present in solution. Ammoniacal silver nitrate solutions containing a trace of alkali (Tollen's reagent) is used in the test. Under the action of oxidizing agents, the glycosidic linkages uniting the individual glucose units of the cellulose are cleaved, which results in shorter chain molecules and hence an increase in the reducing power of the cellulose.

22. In the article "Utilization of 'Pore Spaces' of Semipermeable Membranes," William Moor was interested in making deposits of silver films on cellophane. In using ammoniated silver and acid sucrose solutions and also the Rochelle salt process "a brown deposit began forming in the membrane almost at once, the color depth increasing and gradually changing to a metallic greyish black. Examination of the brown deposit seemed to indicate that it was composed of finely divided metallic silver."³⁴ The author, being mainly interested in photography, worked mostly with the photosensitive silver salts in which he mentioned that a definite arrangement of the metallic silver granules was always found upon exposure and development. This arrangement of silver granules would probably aid the study of the structure of various membrane materials since it was dependent or varied with the different materials used. His procedure could be used "wherever the product of the reaction is less soluble than the reacting substances."³⁴ "It was thought that this process . . . provides a tool that possibly may not have occurred to those investigating the nature of permeable or semipermeable membranes."³⁴

23. Cellophane is effective for screening colloidal silver particles which vary from 1.5 to 3 μ in diameter. "The action of cellophane is to retard the movement of colloidal silver and zinc, in particular to prevent the migration of silver in low molecular weight form by reducing it to metallic silver."¹⁵ "The absorbed silver in the cellophane in equilibrium with 36% potassium hydroxide was about 0.050 mg/70 mg cellophane."¹⁵

CELLOPHANE IN THE SILVER-ZINC CELL

24. Possible beneficial areas of exploration for improving the understanding of the function of the cellophane membrane in the silver-zinc battery are considered in the following paragraphs.

a. Charge of the silver ions in KOH. Dissolved silver oxide in KOH is believed to be in the form of negatively charged ions, "probably a polynuclear anionic complex."² In the Brooklyn Polytechnic Institute Report (Aug. 1954) the existence of different species of silver was suggested, and the main species was believed to be negatively charged, since in an experiment the darkest color on the filter paper appeared near the anode.¹⁵ Perhaps further study might indicate the percentage of negative and positive (Ag^+) silver ions and how complex ions might be formed before the silver oxide is reduced to a metallic form causing high conductance and loading up in the cellophane.

b. Charge on the cellophane. Cellulose is assumed to be negatively charged as a result of the sorption of negative hydroxyl ions or the ionization of positive ions from its surface groups. Because of this cellulose might act as a selective ion barrier in which it would discourage negatively charged particles. Cellophane likewise would probably be slightly cation permeable, as are the membranes of high molecular substance with attached carboxyl or acid groups. Perhaps further investigation might indicate what influence cellophane has on positive and negative silver ions or on the penetration and treeing of zinc.

c. Structure of cellophane. Literature read did not reveal the actual differences between cellulose and cellophane other than to mention that it was regenerated by a process which changed its molecular weight, orientation, and structure, making it more active chemically. Also, the literature did not establish whether cellophane was a gel or a porous media. In any case, the structural formula was not given for cellophane as it had been given for cellulose.

d. Pore size of cellophane. Most sources are in agreement that the pore diameter is approximately $30 \text{ \AA}$, although they do not all agree that cellophane is a porous material. In the Brooklyn Polytechnic Report it states that although ions $10,000 \text{ \AA}$ diameter cannot pass through, ions of $1000 \text{ \AA}$ can.¹⁵ If this is the case, then consideration of pore diameter ($30 \text{ \AA}$ for cellophane) seems to be of little worth even when the effect on pore structure of swelling is considered. As it has been pointed out, too much swelling may cause zinc deposits or may weaken its structure considerably.

e. Cellophane in KOH. Perhaps it would be possible to test for the presence of cellophane to determine the extent to which it is dispersed in solution and would thus be able to interact with the silver particles when present. The amorphous regions of the cellophane could disperse leaving what would appear to be the original untouched separator. One might also determine if and how the presence of ZnO contributes to the dispersion of cellophane. Degradation during alkaline hydrolysis is measured by weight loss, viscosity, tensile strength, and elongation changes.

f. Concentration of KOH. Determination of the effect of different concentrations of KOH on the deposition of silver and the deterioration of cellophane would be worth while. One might also vary the current and ZnO content and at the same time note any changes in membrane potential and resistance. An increase in KOH concentration making more OH^- groups available would probably increase the solubility of silver oxide $\text{Ag}_2\text{O} + 2\text{OH}^- \rightarrow 2\text{AgO}^- + \text{H}_2\text{O}$. As silver ions are released, the degradation of cellophane likewise would increase. The solubility of silver oxide at higher concentrations of the alkaline electrolyte might be determined if this hasn't already been done.

g. Metallic silver. Have X-ray diffraction studies conclusively revealed that when silver migrates and saturates the cellophane that all of it is reduced to the metallic state? What exactly occurs to the cellophane when silver is deposited on it? If cellophane is partially oxidized and contains carbonyl and carboxyl groups, then the reaction $\text{RCOO}^- + \text{Ag}^+ \rightleftharpoons \text{RCOOAg}$ might occur. Cations could probably be bound to the cellophane through the weakly acidic functional groups. Since silver oxide is soluble, then is it not possible that it could undergo some sort of decomposition in the KOH so that the product is metallic silver? Dirkse points out that when $\text{Ag}(\text{OH})_2^-$, the predominant solute species, undergoes decomposition, the dark insoluble material which results is probably silver. "If it is silver, this could account for the deposits of silver on the separators in silver-alkaline cells."¹¹

Perhaps this dark insoluble material or metallic silver resulted from interaction between the silver ions and portions of the cellophane (amorphous regions or low molecular fragments) which had dispersed into the KOH electrolyte.

h. Silver oxide electrodes. If oxygen is evolved at the electrode, then this might increase the silver ion content of the electrolyte, making the deterioration of cellophane more rapid. Possibly the oxygen reacts with the cellophane to form carboxyl groups which then react with the silver ions. A study of the stability and solubility of silver oxide electrodes in the presence of cellophane would aid the separator study for they undoubtedly play a role in influencing the degradation of cellophane.

i. Species of silver. Dirkse indicated that $\text{Ag}(\text{OH})_2^-$ was the predominant solute species given by both Ag_2O and AgO .¹ Previously, Shair had indicated that the peroxide component was the most damaging to cellulosic separators. According to his report, the separator had to act as a barrier to silver ions while being inert to silver peroxide at the same time. Thus, attempts were made to diminish the peroxide component.⁴⁶

j. Zinc. Evidently, cellophane does not prevent the diffusion of zinc as was demonstrated by an experiment at the Brooklyn Polytechnic Institute by the Chemical Engineering Department.⁴ Since cellophane degrades faster in $\text{KOH} + \text{AgO}$ than in $\text{KOH} + \text{AgO} + \text{ZnO}$, then the ZnO must somehow retard the reduction of Ag_2O to metallic silver (zinc probably takes up hydroxyl ions). It might be helpful to determine if a silver-zinc complex ion is formed which would reduce the solubility of the silver oxides. Another useful study might delve into the mechanism of dendritic zinc growth or treeing in which structural imperfections also might be determined by studying the zinc's directional penetration into the cellophane.

k. Separator materials. Various studies could be done to determine whether different membranes react with dissolved silver oxides or whether they catalyze its decomposition. It might be possible to determine how the chemical composition of the separator material affects the amount of silver deposited on it and the amount of degradation it undergoes. Likewise, it would be helpful to compare a material which does not suffer much degradation from silver ions in KOH (i.e., polyethylene and acrylnitrils--very porous) with a material such as cellophane. One might also note and compare the degree of zinc deposition and treeing in various membranes.

1. Reactions with cellophane. According to a recent study, two types of reactions challenge the chemical resistance of cellophane: "first, by the hydrolytic action of the electrolyte; and second, by the oxidative action of various silver containing entities. While the oxidative action is most likely influenced by the passage of electric current, the hydrolytic attack occurs continuously during the entire period of contact between separator and electrolyte."²⁹ On page six of that report it states that "When the cellulose chains are hydrolyzed, not only do they become shortened, but they are also modified in the nature of their dependent or side groups. These become more polar, particularly if any degree of oxidation is involved, and a transition from hydroxyl to carboxylic acid group ensues."²⁹ A fuller discussion and literature review of the reactions of silver with cellophane appears in the cellophane and silver section of this NOLTR.

m. X-ray diffraction and radioactive isotopes. These two methods have been used in silver oxide-zinc alkaline battery studies. R. C. Shair evidently used X-ray diffraction to determine metallic silver on cellophane, according to his Dissertation Thesis, Brooklyn Polytechnic Institute, June 1954. References for work with radioactive isotopes (see Bibliography) include those by Palágyi, Dirkse and Vander Lugt, and Meltzer, Weiss, et al. Diffusion studies with radioactive isotopes have encountered various difficulties since reactions occur between silver and cellophane and radioactive deposits form on the walls and electrodes.

n. Additional references. While this literature study is reasonably complete as far as material available in the NOL library is concerned, there certainly are many other references that bear upon the subject of this report. Some of these are listed in Appendix I.

CONCLUSIONS

25. A separator study on cellophane would be aided by having considerable knowledge of the chemical reactions and the forms of silver and zinc found in KOH in addition to a knowledge of the structure of cellophane itself and the changes it undergoes during reactions. Then a study of the mechanisms of separation would be more revealing. A team of scientists, including an organic chemist, physical chemist, physicist, and/or laboratory technician, could undertake a separator study quite effectively and efficiently.

BIBLIOGRAPHY

1. Amlie, P. F., and Rüetschi, P., "Solubility and Stability of Silver Oxides in Alkaline Electrolytes," J. Electrochem. Soc. 108, 813 (1961).
2. Bieber, H. H., Bruins, P. F., and Gregor, H. P., "Silver Peroxide-Zinc Alkaline Cells Polymeric Membrane Separators," Ind. Eng. Chem. 50, 1273 (1958).
3. Brandenberger, J. E., "Notes on Cellophane," J. Franklin Inst. 226, 797 (1938).
4. Bruins, P. F., et al, "Investigation of Battery Separator Materials," Quarterly Reports under contracts DA-36-039-sc-5425, 70118, and 73120: 9th (Apr 1953), 21st (May 1956) and 25th (June 1957) Prepared by Chemical Engineering Department, Polytechnic Institute of Brooklyn (New York) NOL Library Nos. U-73228, U-87390 and U-95796.
5. Burk, R. E., and Grummitt, O., (eds.), Chemistry of Large Molecules (Interscience Publishers, Inc., New York, 1945), "Cellulose and Its Derivatives" by Emil Ott, p. 243.
6. Clark, G. L., "Cellulose as It Is Completely Revealed by X Rays," Ind. Eng. Chem. 22, 474 (1930).
7. Craig, L. C., and King, Te Piao, "Fractional Dialysis with Cellophane Membranes," J. Am. Chem. Soc. 78, 4171 (1956).
8. Craig, L. C., and Konigsberg, W., "Dialysis Studies III. Modification of Pore Size and Shape in Cellophane Membranes," J. Phys. Chem. 65, 166 (1961).
9. Creutz, E., and Wilson, R. R., "Absorption of Water by Films of Cellophane and Polyvinyl Alcohol," J. Chem. Phys. 14, 725 (1946).
10. Dirkse, T. P., and Wiers, B., "Stability and Solubility of Silver Oxide," J. Electrochem. Soc. 106, 284 (1959).
11. Dirkse, T. P., and Vander Lugt, L. A., "Silver Migration and Transport Mechanism Studies in Silver Oxide-Zinc Batteries," Quarterly Technical Progress Reports 1 - 3, May 1962 - Feb 1963, under Contract No. AF 33(657)-8689. Prepared by Calvin College (Michigan) NOL Library Nos. U-139142, U-139616, and U-140135.

12. Farmery, H. K., and Smith, W. A., "Some Material Problems in the Silver-Zinc Secondary Battery," Preprint of paper delivered at Third International Battery Symposium (Bournemouth, England) Oct. 1962.
13. Fansler, Kevin S., Separator study notebooks, NOL Nos. 96-6296 and 96-6424.
14. Farrar, J., and Neale, S. M., "Distribution of Ions Between Cellulose and Solutions of Electrolyte," J. Colloid Sci. 7, 186-95 (1952).
15. Gregor, H. P., et al, "A Study of the Application of Ion Exchange to Electric Batteries," Final Progress Report under Contract No. NObs-62383 (June 15, 1953 to Aug. 31, 1954) Prepared by Polytechnic Institute of Brooklyn (New York).
16. Harrap, B. S., and O'Donnell, I. J., "Permeability of Cellophane Membranes to Sodium Dodecyl Sulfate Solutions," J. Phys. Chem. 58, 1097-9 (1954).
17. Haskell, V. C., and Owens, D. K., "The Development of Molecular Orientation During Formation of Cellulose Films from Viscose," J. Appl. Polymer Sci. 4, 225-30 (1960).
18. Hauser, E. A., "What the X Ray Tells Us of the Structure of Cellulose," Ind. Eng. Chem. 21, 124 (1929).
19. Heuser, Emil, Cellulose Chemistry, (John Wiley & Sons, Inc., London, 1944).
20. Horio, M., et al, "Viscoelastic Properties of Several High Polymers," J. Appl. Phys. 22, 966-70 (1951).
21. Hyden, W. L., "Manufacture and Properties of Regenerated Cellulose Films," Ind. Eng. Chem. 21, 405 (1929).
22. Inskeep, G. C., and Van Horn, P., "Cellophane," Ind. Eng. Chem. 44, 2511 (1952).
23. Johnson, Cuta, and Garrett, "Solubility of Silver Oxide in Water, in Alkali and in Alkaline Salt Solutions. The Amphoteric Character of Silver Hydroxide," J. Am. Chem. Soc. 55, 2311 (1933).
24. Kawasaki, K., "The Variation of Electrical Resistance of a Polymer as a Function of the Extent and Nature of Sorbed Water," J. Colloid Sci. 16, 405-10 (1961).
25. Madras, S., McIntosh, R. L., and Mason, S. G., "A Preliminary Study of the Permeability of Cellophane to Liquids," Can. J. Res. 27B, 764 (1949).

26. Marcheasault, R. H., (ed.), "Proceedings of the Fourth Cellulose Conference," J. Polymer Sci., Part C, Polymer Symposia No. 2, 1963.

27. Mark, H., "Structure of High Molecular Substances (Intermicellar Hole and Tube System in Fiber Structure)," J. Phys. Chem. 44, 764-88 (1940).

28. McBain, J. W., and Kistler, S. S., "Ultrafiltration as a Test for Colloidal Constituents in Aqueous and Non-Aqueous Systems," J. Phys. Chem. 35, 130 (1931).

29. Meltzer, T. H., "Alkaline Battery Separator Study," Quarterly Report No. 1 under Contract No. NAS-5-2860; also see Reports No. 2 (by C. Garvin and E. Weiss), No. 3 (by C. G. Oberholzer and E. Weiss) and No. 4 (by C. G. Oberholzer, A. J. Salkind, and E. Weiss) Prepared by Carl F. Norberg Research Center, Electric Storage Battery Company (Yardley, Pa.), June 28, 1962 - June 1963.

30. Mendelsohn, M., "Separator for Electric Battery," Patent No. 2,915,579, patented Dec. 1, 1959.

31. Middlehurst, D., and Weller, R., "Polarizing Properties of Cellophane," Rev. Sci. Instr. 11, 108 (1940).

32. Mitchell, R. L., "Cellulose, Raw Material for Cellophane," Ind. Eng. Chem. 47, 2370-3 (1955).

33. Monaghan, White, and Urban, "A Comparison of the Electrophoretic Velocities of Cellophane and Colloidion Suspensions with Electro-osmotic Velocities Through Membranes of the Same Material," J. Gen. Physiology 18, 523 (1935).

34. Moor, W., "Utilization of 'Pore Spaces' of Semi-permeable Membranes," Science 100, 494 (1944).

35. Morton, T. H., "The Dyeing of Cellulose with Direct Dyestuffs. The Importance of the Colloidal Constitution of the Dye Solution and of the Fine Structure of the Fibre," Trans. Faraday Soc. 31, 262 (1935).

36. Neale, S. M., "Diffusion of Dyes Through Cellophane," Trans. Faraday Soc. 44, 1027-30 (1944).

37. Neale, S. M., "Absorption of Dyes by Cellulose VIII. Analysis of Ionic Distribution by Means of Diffusion Potentials," Trans. Faraday Soc. 43, 325-31 (1947).

38. Othmer, Kirk, Encyclopedia of Chemical Technology
3, (Interscience Encyclopedia Inc., New York, 1949) pp. 280-
292.
39. Ott, Emil, Spurlin, Harold M., and Grafflin, Mildred
W., Cellulose and Cellulose Derivatives, Parts I - III; High
Polymers 5, (Interscience Publishers, Inc., New York, 1955).
40. Palágyi, T. Z., "Investigations on the Silver-Zinc
Alkaline Storage Battery by the Aid of Radioactive Isotopes,"
J. Electrochem. Soc. 106, 846 (1959).
41. Palágyi, T. Z., "Investigations on the Silver-Zinc
Storage Battery with Radioactive Zn⁶⁵ Isotope," J. Electrochem.
Soc. 108, 201 (1961).
42. Palágyi, T. Z., "Investigations on the Silver-Zinc
Storage Battery with Radioactive Ag¹¹⁰ Isotope," J. Electrochem.
Soc. 108, 904 (1961).
43. Preston, R. D., "Fabrillar Units in the Structure of
Native Cellulose," Discussions Faraday Soc. 11 (1951).
44. Prideaux, E. B. R., "Mobility of Quinine Ions with
Some Notes on the Permeability of Cellophane," Trans. Faraday
Soc. 38, 121-8 (1942).
45. Ranby, B. G., "The Colloidal Properties of Cellulose
Micelles," Discussions Faraday Soc. 11 (1951).
46. Shair, R. C., Bruins, P. F., and Gregor, H. P.,
"Separators for the Silver Peroxide-Zinc Alkaline Battery,"
Ind. Eng. Chem. 48, 381-5 (1956).
47. Shair, R. C., "Ion Exchange Membranes and Their
Application to the Silver-Peroxide-Zinc Battery," Dissertation
Thesis, Brooklyn Polytechnic Institute (New York) June 1954.
48. Sharples, A., "Hydrolysis of Cellulose and Its Rela-
tion to Structure," Trans. Faraday Soc. 53, 1003-13 (1957).
49. Silverman, S., "Concerning the Polarizing Properties
of Dyed Cellophane Films," Rev. Sci. Instr. 12, 212 (1941).
50. Simril, V. L., and Smith, S., "Sorption of Water by
Cellophane," Ind. Eng. Chem. 34, 226 (1942).
51. Sisson, W., "X-Ray Studies of Crystallite Orientation
in Cellulose Fibers. III," J. Phys. Chem. 44, 513 (1940).

52. Stamm, A. J., "Diffusion of Water into Uncoated Cellophane I. From Rates of Water Vapor Adsorption and Liquid-Water Adsorption," J. Phys. Chem. 60, 76-82; "From Steady State Diffusion Measurements," 60, 83-86 (1956).
53. Stoops, W. H., "Dielectric Properties of Cellophane," J. Am. Chem. Soc. 56, 1482 (1934).
54. Teorell, T., "Ionic Transference Numbers in Cellophane Membranes," J. Gen. Physiology 19, 917 (1936).
55. Ticknor, L. B., "On the Permeation of Cellophane Membranes by Diffusion," J. Phys. Chem. 62, 1483 (1958).
56. Tuwiner, Sidney B., Miller, Lawrence P., and Brown, W. E., Diffusion and Membrane Technology (Reinhold Publishing Corp., New York, 1962), Ch. 10, "Cellulose Membranes."
57. White, Monaghan, and Urban, "Electrical Factors Influencing the Rate of Filtration of Aqueous Electrolyte Solutions Through Cellophane Membranes," J. Gen. Physiology 18, 515 (1935).
58. Wise, Louis E., Wood Chemistry (Reinhold Publishing Corp., New York, 1946).
59. Wright, M. L., "Membrane Potentials for Keratin and Cellophane and the Meyer-Teorell Theory," J. Phys. Chem. 58, 50 (1954).
60. Voyutskii, S. S., Shapovalova, A. I., and Pisarenko, A. P., "Adhesion of High Polymers. 3. Effects of the Size, Shape, and Polarity on Adhesion of Cellophane," Rubber Chem. and Tech. 31, 712-18 (1958).
61. "British Cellophane Ltd.," Chem. and Ind., June 28, 1958, pp. 784-5.

APPENDIX I

Supplemental Bibliography of Articles of Probable Interest
Which Are Not Available at NOL

- Acta Pharmacol et Toxicol 5, 173-8 (1949)
"Cellophane for Ultrafiltration"
- Chem. Listy 49, 826-33 (1955)
"Properties of Semipermeable Cellophane Membranes"
- Das Papier 9, 588-93 (1955)
"Structure of Papers and Regenerated Cellulose Films"
- French Patent #1,230,281
"Porous Membranes Applicable as Separators in Alkaline Storage Batteries"
- German Patent #1,094,829
"Separator for Silver-Zinc Storage Batteries"
- German Patent #1,030,407 (May 22, 1958)
"Insulating Separator for Silver-Zinc Storage Batteries"
- Japan 90, 69 (1960)
"Separator for Alkaline Storage Batteries--Cellophane"
- Japan 18, 91 (1961)
"Cation-exchange Resins--Cellophane"
- J. Chim. Phys. 53, 278-83 (1956)
"Research on Osmosis II"
- J. Biol. Chem. 134, 701-7 (1940)
"The Preparation of Cellophane Membranes of Graded Permeability"
- J. Univ. of Bombay 17A, #24, 40-7 (1948)
"Swelling of Cellulose"
- Kolloid Zhur 16, 381-6 (1954)
"Diffusion of Various Substances Through Hydrocellulose Films"
- Referat Zhur Khim, 1954, #39339
"Relation Between Sorption and Swelling of Cellophane"

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Zinc		ZINC		

Naval Ordnance Laboratory, White Oak, Md. (NOL technical report 63-225) CHARACTERIZATION OF CELLOPHANE AS AN IONIC BARRIER, by Claudia C. Evans. 11 March 1964. 18p. illus. BuWeps task RUTO 3E000/212. UNCLASSIFIED Cellophane, a gel developed from crystalline alpha-cellulose, has been used as an ionic barrier (battery separator) in electric batteries with outstanding success for many years. Understanding the mechanism of the cellophane action in ionic barrier applications could lead to the development of superior ionic barriers.	1. Cellophane 2. Batteries - Separators I. Title II. Evans, Claudia C. III. Project Abstract card is unclassified.	1. Cellophane 2. Batteries - Separators I. Title II. Evans, Claudia C. III. Project Abstract card is unclassified.	1. Cellophane 2. Batteries - Separators I. Title II. Evans, Claudia C. III. Project Abstract card is unclassified.
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