OBJECTIVE:
The work has sought to understand the mechanism of dissolution on the DMSO/PF solvent. More recently, the emphasis has been directed toward understanding aspects of the system which would be particularly important in possible commercial applications.

BUDGET:
None specified.
Expenses for 1976-77 fiscal year are approximately $2,800.

Only $500 of expenses have been charged during past six months.

SCHEDULE: See last comment above - Related work has been progressing within Project 3335.

SUMMARY OF RESULTS AND PLANS FOR FUTURE WORK: The only recent activity has been related to correspondence and details concerning our patent application. No plans exist for future work.
THE INSTITUTE OF PAPER CHEMISTRY
QUARTERLY RESEARCH REPORT
Prepared by D. C. Johnson, Project Leader

DIVISION: Natural Materials and Systems

DATE: Jan. 18, 1977

PROJECT NO.: 3155 - "Commercial Applications of Dimethyl Sulfoxide/
Paraformaldehyde Cellulose Solvent"

Class: FE

OBJECTIVE:
The work has sought to understand the mechanism of dissolution in the DMSO/PF
solvent. More recently, the emphasis has been directed toward understanding
aspects of the system which would be particularly important in possible com-
mmercial applications.

BUDGET:
None specified.

Expenses for current fiscal year are $2,540 with only $220 of that
amount charged during the last quarter.

SCHEDULE:
Work in this general area is being concentrated within Project 3335.

SUMMARY OF RESULTS AND PLANS FOR FUTURE WORK:
Earlier work has been published in Applied Polymer Symposium, No. 28, 931(1976).
A related paper, based to a greater degree on thesis work, will appear in
Cellulose Chemistry and Technology in early 1977. At the present time, it
appears that little future work will be carried out on this project because
of the on-going efforts in Project 3335.
The work has sought to understand the mechanism of dissolution in the DMSO/PP solvent. More recently the emphasis has been directed toward understanding aspects of the system which would be particularly important in possible commercial applications.

It was possible to sustain a modest amount of research in July because of help provided by a summer employee. Since then activity has been slight.

Analysis of methylcellulose samples by liberation of formaldehyde indicated a wide range of methylcellulose content, but more important was the finding that DMSO concentrations of up to 10% can be prepared using lower P-cellulose ratios than are required at 1-3% concentrations.
The amount of dimethyl sulfoxide retained in solid methylol cellulose was determined using a NMR procedure we developed. These values ranged from 20-29%. It is interesting that methylolcellulose having a DS of 1.0 with an equimolar amount of DMSO to stabilize methylol groups would have a DMSO content of 29%.

Future Work: As work gets under way in a related cooperative project, it is expected that activity in this project will increase somewhat depending on available manpower. The formaldehyde analysis problem should be resolved soon.
PROJECT NO: 3155 - "Commercial Applications of Dimethyl Sulfoxide/Paraformaldehyde Cellulose Solvent"

OBJECTIVE: The work has sought to understand the mechanism of dissolution in the DMSO/PF solvent. More recently, the emphasis has been directed toward understanding aspects of the system which would be particularly important in possible commercial applications.

BUDGET: Expenses from July 1975 through May, 1976 total $12,555.

April-June (3 months) expense was about $1,700.

SUMMARY OF RESULTS AND PLANS FOR FUTURE WORK: An important development related to our work on this project has been the interest of a subsidiary of one of our member companies in a cooperative project. The proposal has been written and submitted. It focuses on the use of the solvent for preparing certain cellulosic films.

Within the scope of the present project, we would like to develop a clearer understanding of the properties of methylol cellulose than presently exists. Such information is desired because of its critical role in the dissolution process. We plan to isolate and characterize methylol cellulosics prepared in various ways.
We hope to examine the relationship between solubility and degree of substitution (D.S.). This work should aid in determining the ease of controlling the D.S. level in the system. It may also help us learn whether formaldehyde use in the solvent system can be made more efficient.
PROJECT NO. 3155 - "Commercial Applications of Dimethyl Sulfoxide/Paraformaldehyde Cellulose Solvent"

OBJECTIVE:

The work has sought to understand the mechanism of dissolution in the DMSO/PF solvent. More recently, the emphasis has been directed toward understanding aspects of the system which would be particularly important in possible commercial applications.

BUDGET:

Expenses from July through March total = $11,151
In the last three months about $2000 spent.

SCHEDULE:

The level of activity has been rather low during the last three months compared with the earlier part of the fiscal year. This was anticipated because of other demands on available staff time.

SUMMARY OF RESULTS AND PLANS FOR FUTURE WORK:

Three samples of paraformaldehyde/DMSO suspensions were specially prepared by Celanese Chemical Co. and shipped to us. Attempts to use these to dissolve cellulose were all unsuccessful. The major problem appears to be the high decomposition temperature of Celanese paraformaldehyde.

A methylolxylan was isolated by freeze-drying a DMSO/PF solution of an elm xylan. The apparent D.S. was about 0.5 according to formaldehyde analysis. This helps to confirm the previously indicated application of the solvent to other polysaccharides besides cellulose. Further work was also done on the characterization of methylolcellulose samples to gain more experience with the analytical procedure for formaldehyde content.
Seminars on the cellulose solvent system were presented during the past quarter at the laboratories of Tee Pak Inc. (subsidiary of Continental Can Co., Inc. in Danville, Illinois and at American Cyanamid Co. in Stamford, Conn.

Part of the recent effort has been devoted to preparation of the patent application covering the solvent system which has been filed.

On the basis of fiber spinning work done by International Paper Co., they proposed a more intensive joint program of research to thoroughly evaluate the fiber-spinning potential of DMSO/PF. They suggested equal funding by them and the Institute. We have not accepted their proposal but we may propose an alternative program which would examine several factors of probable importance in any commercial use of the cellulose solvent. This latter program might be funded by a group of companies.
PROJECT NO.: 3155 - "An Investigation of the Cellulose Solvent Dimethyl Sulfoxide/Paraformaldehyde Factors Influencing Dissolution and Its Potential as a Pulping Agent

OBJECTIVE:
The work has sought to understand the mechanism of dissolution in the DMSO/PF solvent. In recent months, application of the solvent has been extended to a wider variety of materials. Feasibility of commercial application is receiving attention.

BUDGET:
Expenses from July through December totaled about $9,200. Expenses during fiscal 1975 were $8,020.

SCHEDULE:
A plan for future work will be discussed soon.

SUMMARY OF RESULTS AND PLANS FOR FUTURE WORK:
International Paper Company has been interested in the solvent system as a possible alternative to the viscose spinning process. I visited their laboratories at Tuxedo Park at the end of October to learn about spinning trials they had conducted. Their results were encouraging; they were indeed able to spin fibers successfully in three out of seven batches. More recently, I learned that strength tests on these fibers were also encouraging. I was told that, in one run, the properties were very close to those of conventional rayon. Formaldehyde content in the fibers was very low, between 90 and 400 parts per million.
We were visited in November by a representative (Gary Kastor) of Celanese Corporation because of their position as a major manufacturer of paraformaldehyde. The discussion was helpful, and suggestions were offered which may be of value in promoting a more efficient use of formaldehyde in the dissolving process. We have begun to follow up some of these suggestions in our experimental work. In addition, Celanese is going to try to provide us with a sample of a solution of paraformaldehyde in dimethyl sulfoxide which will be analogous to their Formcel solutions (which involve alcohols).

Considerable effort was put into preparation of our patent application after receiving a rough first draft from our lawyers. As I understand it, the time remaining for us to submit this application is growing short.
PROJECT NO. 3155 "An Investigation of the Cellulose Solvent Dimethyl Sulfoxide/Paraformaldehyde Factors Influencing Dissolution and its Potential as a Pulping Agent"  Class: FE

OBJECTIVE: The work has sought to understand the mechanism of dissolution of cellulose in the DMSO/PF solvent. In recent months, application of the solvent has been extended to a wider variety of materials. Feasibility of commercial application is receiving greater attention.

BUDGET: Fiscal 1975 expenses totaled $8,020. Expenses from July through September were $4,843.

SCHEDULE: The direction of future work on this project will be evaluated during the next month. International Paper Company is planning to evaluate the feasibility of the solvent for fiber spinning using their rayon equipment. Our future work plan may be influenced by their evaluation.

SUMMARY OF RESULTS AND PLANS FOR FUTURE WORK:

We have tried to induce cross-linking of the methylolcellulose by regeneration into acidic media, but only cellulose is formed. This serves to further dramatize the unusual nature of this solvent system. Regeneration into methanol is being studied to see whether a cellulose derivative is produced.

Further trials to dissolve chitin chitosan have been unsuccessful. An elm xylan has shown enhanced solubility in DMSO/PF versus DMSO alone.
Most of our recent efforts have focused on preparation of concentrated (3-6%) solutions using dissolving pulp samples provided by International Paper Company. Several runs were carried out using a closed system. Stirring was found inadequate for reaching the desired concentration levels. We have since been able to prepare 6% solutions in an open system with good mechanical stirring. International representatives have visited us (late September) and were encouraged with our results. They are proceeding with efforts to evaluate fiber-spinning potential of the system. I will visit them again in late October.

A seminar was presented on the solvent system at International (Tuxedo Park) in September, and a similar presentation will be made at St. Regis Technical Center in late October.

Future plans will depend, in part, on results of International's evaluation. We continue to receive expressions of interest and ideas concerning practical applications from many sources. Representatives of both Celanese (paraformaldehyde source) and Crown Zellerbach (DMSO source) have expressed interest in our progress.

Certain additional experiments may be needed to fortify our potent application but the nature of these is not yet clear.
PROJECT NO.: 3155 -- An Investigation of the Cellulose Solvent Dimethyl Sulfoxide-Paraformaldehyde Factors Influencing Dissolution and Its Potential as a Pulping Agent

OBJECTIVE:
The work seeks to understand the mechanism of dissolution of cellulose in the DMSO/PF solvent. Recently, we have begun to explore a variety of applications of the solvent.

BUDGET:
Through May the fiscal year total expense was $6,391.43.

SCHEDULE:
After presenting a portion of this work and related student research at the Cellulose Conference in May, a number of areas were defined for further research and priorities assigned. Certain additional experiments may be necessary in connection with our patent application.

SUMMARY OF RESULTS AND PLANS FOR FUTURE WORK:
During the last quarter a paper was completed covering work done within the scope of this project as well as related thesis work by Nicholson. This paper was released to the membership and was presented at the Eighth Cellulose Conference in May and will be published in the Symposium edition of J. Polymer Science.

We have continued work in several areas. One of these involved treating sheets under conditions where surface cellulose might be partly dissolved
and later regenerated. Strength measurements were carried out in Wink's group, but the results suggested that very little change had taken place. An alternate approach involving deposition of dissolved cellulose at the surface will also be examined. Some related work is going forward in the Container Section.

We have also been looking at the application of the solvent to dissolve other materials. Specifically, these have included bagasse, thermomechanical pulp, and chitin. Thus far, use of the solvent under normal conditions does not dissolve appreciable amounts (5% or more) of any of these samples. These resistant materials will be treated with the solvent system using a suitable pressure vessel to eliminate loss of formaldehyde. These experiments could be important to our patent position.

Work is in progress to assess whether or not cross-linking can be induced in the regeneration step. We intend to explore further the possibility of a cooperative effort with another laboratory to help us evaluate fiber and film formation using the solvent system. We are also preparing copolymer blends by regeneration of dissolved cellulose with another dissolved polymer.

The paper given at Syracuse along with publicity in Chemical and Engineering News have sparked nearly 100 requests for more information. Several of these have indicated possible uses for the solvent system.

A seminar was presented at Hercules Research Center on June 24 at their invitation.

Project Leader: Donald C. Johnson

Class: I (FE)

OBJECTIVE: The work seeks to understand the mechanism of dissolution of cellulose in the DMSO-PF solvent.

BUDGET: During February expenses totaled $972.05 and the fiscal year total through February was $1,519.44. Expenses during March will exceed those of February.

SCHEDULE: Work covered under this project and related student research will be sent to the membership as a publication in April. It will be presented at the Eighth Cellulose Conference in May. There are numerous areas deserving further research and some are cited below.

SUMMARY OF RESULTS AND PLANS FOR FUTURE WORK: We have recently investigated the preparation of the DMSO-PF system using paraformaldehyde (PF) from different commercial sources. This was done to check into previous observations that had revealed problems with certain lots of PF. It now appears that the temperature at which PF decomposes to liberate formaldehyde is quite variable depending on the source and undoubtedly the degree of polymerization and other factors. Certain samples of paraformaldehyde generate formaldehyde in DMSO at such a high temperature that the formaldehyde is swept out of the solution too rapidly and cellulose fails to dissolve. We have shown that these same samples of PF can be used provided that they are thermally decomposed in a separate vessel and the formaldehyde gas is swept into the DMSO-cellulose suspension at the optimum dissolving temperature. Additional NMR studies have shown little difference exists between the solutions of DMSO-PF.
prepared in the latter manner from a variety of PF samples.

Additional experiments focused on the partial dissolution of high yield pulps. A kraft softwood pulp (57.5% yield) and an NSSC hardwood pulp were partially dissolved in the solvent. Infrared spectra pyrolysis-gas chromatography and carbohydrate analyses revealed that the dissolved material contained very little lignin whereas the residual material was rich in lignin and also had a higher ratio of hemicellulose to cellulose.

The research on this project and some related student work is presently being assembled for publication and presentation at the Eighth Cellulose Conference in Syracuse. The project should be continued in the Funded-Exploratory category. Possible experiments could include a brief study of copolymer blends regenerated from the solvent system and a further look at the pulp dissolving mechanism; carbohydrate analyses have raised a question about the material balance in regenerated and residual samples.

Prepared by Donald C. Johnson
THE INSTITUTE OF PAPER CHEMISTRY
QUARTERLY RESEARCH REPORT
Prepared by Don Johnson

DIVISION: Natural Materials & Systems

DATE: January 13, 1975

PROJECT NO.: 3155
Title: Investigation of the Cellulose Solvent Dimethyl Sulfoxide-Paraformaldehyde: Factors Influencing Dissolution and Its Potential as a Pulping Agent
Cooperator: Institute
Project Leader: Donald Johnson

OBJECTIVE:
The work seeks to understand the mechanism of dissolution of cellulose in the dimethyl sulfoxide-paraformaldehyde solvent.

BUDGET:

SCHEDULE: Work covered under this project and related student research is being written for publication, and it will be presented at the Cellulose Conference in Syracuse during the week of May 19th. During the next three months we plan to carry out a few additional experiments to try to better clarify remaining questions about the dissolution process.

SUMMARY OF RESULTS AND PLANS FOR FUTURE WORK: The results were summarized in the preceding quarterly research report (dated October 1, 1974). There has been no further experimental work on this project. Related thesis research, however, has provided additional support for the previously suggested mechanism of dissolution. Specifically, it was found that a solution of cellulose in DMSO-PF could be freeze-dried to give a solid which could be dissolved immediately in dimethyl sulfoxide at room temperature. This fact combined with Raman spectral evidence strongly indicates that the solid resulting on freeze-drying is hydroxymethylcellulose. Since this is a hemiacetal, it would be expected to produce cellulose in any water regeneration step as is observed.
Recently, student research has indicated that certain paraformaldehyde lots from various manufacturers do not work well in one of the cellulose-dissolving procedures. Future work is planned to investigate the reason for this variation within commercial lots of paraformaldehyde.
PROJECT NO.: 3155
Title: Investigation of the Cellulose Solvent Dimethyl Sulfoxide-Paraformaldehyde: Factors Influencing Dissolution and Its Potential as a Pulping Agent
Cooperator: Institute Project Leader: Donald Johnson
OBJECTIVE: The work seeks to understand the mechanism of dissolution of cellulose in the dimethyl sulfoxide-paraformaldehyde solvent.

SUMMARY OF RESULTS AND PLANS FOR FUTURE WORK: As part of our study to determine the major factors which influence the dissolution of cellulose, we have found that the dimethyl sulfoxide-paraformaldehyde combination is quite specific. Attempts to prepare other related solvents have not been successful. The DMSO-PF system can be prepared in various ways, however, and these have been cited in an Invention Record. One of these
involves external generation of formaldehyde gas which is then swept into a heated mixture of DMSO and cellulose.

Nuclear magnetic resonance (NMR) spectra of deuterated DMSO-PF solutions of low DP cellulose, monosaccharides, methanol, and butanol have helped clear up several questions. The actual amount of paraformaldehyde retained in the DMSO during cellulose dissolution is only about 0.3%. The spectra along with recent work by Myron Nicholson offer support for the view that cellulose may react with formaldehyde at the C-6 hydroxyl group. The resulting hemiacetal would be solvolyzed upon cellulose regeneration by pouring into water or methanol. In fact, cellulose is regenerated as cellulose II from the solvent with little apparent degradation. Regeneration in the form of fibers has been successfully achieved, and the fibers appear very similar to cuprammonium rayon when examined under the polarizing microscope.

Limited efforts to dissolve cellulose from wood have not been encouraging. However, substantial amounts of a southern pine kraft pulp (unbleached, 12.5% Klason lignin) and a NSSC poplar pulp were dissolved by the DMSO-PF treatment.

Specific recommendations for further work will be included in the forthcoming report.
Prepared by: Don Johnson

PROJECT NO.: 3155

Title: Investigation of the Cellulose Solvent Dimethyl Sulfoxide-Paraformaldehyde: Factors Influencing Dissolution and Its Potential as a Pulping Agent

Cooperator: Institute

Project Leader: Donald Johnson

OBJECTIVE:
The work seeks to understand the mechanism of dissolution of cellulose in the dimethyl sulfoxide-paraformaldehyde solvent.

BUDGET:

SCHEDULE: A report will be completed as soon as possible.

SUMMARY OF RESULTS AND PLANS FOR FUTURE WORK: As part of our study to determine the major factors which influence the dissolution of cellulose, we have found that the dimethyl sulfoxide-formaldehyde combination is quite specific. Attempts to prepare other related solvents have not been successful. The DMSO-PF system can be prepared in various ways, however, and these have been cited in an Invention Record. One of these
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Specific recommendations for further work will be included in the forthcoming report.

The only work planned for the present quarter is the writing of a complete report on the results obtained.