of DMF. From the fact that the decrease in the yield of FA, MMF and DMF is accompanied with the increase of free amines, it is inferable that MMF and DMF are not produced by the direct methylation of FA.

2) The affect of charge mole ratio NH_3/MeOH: The yield of mono and dimethyl compounds varies in proportion to the mole ratio NH_3/MeOH, but the dimethyl compounds begin to disappear for NH_3/MeOH 1.5. For the low NH_3/MeOH, remarkable amount of trimethylamine (TMA) is produced and MeOH is completely consumed. From this fact, together with the stability of DMF under the compressed CO, we presume that the methylation foregoes the formylation.

3) The effect of CO pressure: It is very interesting that monomethylation does not occur and only dimethylation occurs to some extent in the absence of CO. Moreover, the peculiar phenomenon is found that the methylation proceeds as the rise of CO pressure, whereas it ceases at 400 atm.

4) The effect of catalyst amount and some solvents: AcOK is supposed to be an effective catalyst for the methylation, because a remarkable increase of mono and dimethyl compounds formation is observed even when the trace of this substance is added.

But, above the mole ratio AcOK/MeOH=0.04, the methylation is complete and no more DMF is formed. In the presence of a large amount of NH_3 and MeOH, without catalyst and solvent, the commencement of the pressure drop delays, and the reaction rate is small, but appreciable amount of FA, MMF and DMF is prodused.

When glycerin or water is used as solvent, the yield of MMF and DMF is the same as in the case of AcOK catalyst. So, FA seems to be effective as a solvent.

5) Replacement of FA as the starting material for NH_3: The yield of DMA from NH_3 is larger than that from FA, and the total amount of mono, di, and trimethyl compounds decreases as the increase of CO pressure. So, it seems quite probable that the reaction proceeds in the order of NH_3 → amine → amide.

6) Conclusion: a) Optimum condition. 280°C, CO initial pressure 500 atm., NH_3/MeOH=1.2 (mole ratio), AcOK/MeOH=0.03 (mole ratio), MeOH charge 0.6 *M*/100 c.c. autoclave; yield (in 3 hrs.), DMF42%, MMF 34% (MeOH base). b) The reaction is supposed to proceed by NH_3 → amine → amide ni the liquid phase, where FA serves as the solvent.

Acetylation of Cotton Fabric by the Liquid Phase Method

Waichiro TSUJI, Ryozo KITAMARU and Yasuyoshi SAKAGUHI

Sen-i Gakkaishi (Journal of the Society of Cellulose and Textile Industry, Japan), **16**, 1021 (1960)

Cotton fabrics were acetylated up to a wide degree of substitution by the liquid phase method as reported in the above journal (1957) by Sakurada and Sakaguchi.

In the present study tensile properties of the fabrics were examined before and after acetylation and it was found that under proper conditions the cotton fabric could be acetylated up to high degree by the liquid phase method without lowering the tensile strength.

The preparation method of acetylation bath and its stability, the comparison of various catalyzers and diluents are discussed.

Acetylation of Cotton Fabric by the Semi-Liquid Phase Method (So-Called Padding Method)

Waichiro TSUJI, Ryozo KITAMARU and Yasuyoshi SAKAGUCHI

Sen-i Gakkaishi (Journal of the Society of Cellulose and Textile Industry, Japan), **16,** 1026 (1960)

Cotton fabrics, pretreated with acetic acid, were immersed in the acetylation bath, which consists of acetic anhydride and catalyzer, and squeezed to about 60-70% pick-up and then heated in a closed vessel. During these processes the cotton fabrics are acetylated. In this acetylation method, almost all parts of acetic anhydride contained in fabrics are consumed in the reaction and cotton fabrics are acetylated to about 30 mol% without lowering the tensile strength in a very short time.

This method would be advantageous applied to an industrial continuous acetylation, because the immersion in liquid and the reaction could be finished in an extremely short time.

Studies on the Fibrous Acetylation of Cotton. (III) Some Properties of Acetylated Cotton

Waichiro TSUJI Ryozo KITAMARU and Masazo IMAI

Sen-i Gakkaishi (Journal of the Society of Cellulose and Textile Industry, Japan), **17,** 235 (1961)

Various properties of acetylated cotton, which have been prepared by the method reported in our previous papers were examined in detail. Properties examined are as follows: tensile properties, water and moisture absorption, specific gravity, microscopic structure, thermal and electric properties, abrasion resistance, weathering resistance, resistance to acid, flammability, dyeability, shrinkage by water boiling, soiling and soil removal, *etc.*
