

A Measure of Effective Crosslinks in Formaldehyde-Modified Cotton Celluloses*

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Synopsis

Sol-gel fractions have been measured for cotton celluloses crosslinked with formaldehyde under widely different conditions of reaction and have been employed for estimation of the efficiency of crosslinking in the various processes. Most efficient utilization of formaldehyde for insolubilization of molecular chains is indicated for an aqueous process (form W') and least efficient utilization is indicated for a nonaqueous process (form D'), the difference in efficiency being approximately a factor of 40. Interpretation of sol-gel data has been made relative to a model assuming random reaction of crosslinking agent throughout the cotton cellulose and by relationships developed by Charlesby and Pinner and by Shultz. This leads to estimates of relative numbers (moles) of effective chain elements per gram, ν_e (i.e., twice the number of effective crosslinks), which decrease in the following sequence for cottons at the 0.20% level of formaldehyde (i.e., 6.7×10^{-6} mole/g.): aqueous process, higher formaldehyde concentration (W', $\nu_e = 4.8 \times 10^{-5}$), vapor process (V, $\nu_e = 1.75 \times 10^{-5}$), bake-cure process (C, $\nu_e = 1.37 \times 10^{-5}$), aqueous process, lower formaldehyde concentration (W, $\nu_e = 0.95 \times 10^{-5}$), nonaqueous process (D, $\nu_e = 0.03 \times 10^{-5}$).

INTRODUCTION

Although the evidence for network structure in cotton cellulose modified by polyfunctional agents is predominantly circumstantial, it is, nevertheless, abundant and generally consistent. For the most part it is agreed¹ that these modified cotton celluloses involve a multitude of crosslinks together with varying proportions of intramolecular linkages, substituents, and, in some cases, deposited resin. Considerable evidence has been accumulated to indicate that the distribution of crosslinks within the cotton fibers varies with the process of introduction,²⁻⁴ that the crosslink is not monomeric,⁵⁻⁷ and that only a fraction of the reacted agent is involved in intermolecular crosslinking.^{8,9} Thus, two primary basic parameters which characterize the network structure of cotton cellulose are (a) frequency or concentration of crosslinks and (b) distribution of crosslinks. Unequivocal quantitative

* Presented in part at the Spring Meeting of The Fiber Society at Williamsburg, Virginia, May 1966.

measurement of each of these factors is a matter of major concern as an approach to understanding the relationships among the process of chemical treatment, structure of crosslinked cotton cellulose, and physical performance properties of the fiber, yarn, or fabric.

The extension of the qualitative concept of network structure in cotton cellulose to quantitative formulation has been hampered by lack of quantitative experimental methods as well as the complexities in theoretical treatment which arise from the morphology of the fiber structure and the semicrystalline nature of the cotton cellulose.^{9,10} It is evident that quantitative studies might well proceed with measurements of sol-gel fractions in crosslinked cotton celluloses and that such measurements might lead to quantitative values for frequency of crosslinks.

This report describes an examination of the distribution of formaldehyde crosslinks among cotton cellulose molecules as a function of the level of the

TABLE I
Crosslinking Processes

Designation	Reagents	Procedure ^a	Reference
Form W	7.6% CH ₂ O ^b 12.2% HCl 2.2% CH ₃ OH 78.0% H ₂ O	Reaction in bath at room temperature	12
Form W'	16.0 CH ₂ O ^c 14.6% HCl 69.4% H ₂ O		
Form C	1.0-7.5% CH ₂ O ^b 0.4-2.0% MgCl ₂ ·6H ₂ O 90.5-98.6% H ₂ O	Padded in bath, dried, cured at 180°C. for 1 min.	13
Form D	5.5% CH ₂ O ^b 5.5% HCl 71.3% CH ₃ COOH 1.6% CH ₃ OH 16.1% H ₂ O	Reaction in bath at room temperature	14
Form D'	9.8% CH ₂ O ^c 6.6% HCl 66.0% CH ₃ COOH 17.6% H ₂ O		
Form V	CH ₂ O vapor ^c HCl vapor Ambient moisture	Reaction in vapors at room temperature	15

^a All samples rinsed thoroughly in hot water, dilute alkali, and/or put through a laundry cycle.

^b 37% Formalin containing 11% methanol.

^c Paraformaldehyde.

agent and the process of reaction. Quantitative measurements of the distribution of crosslinks among cellulose molecules have been undertaken based on the determination of soluble cellulose as described by Bullock et al.¹¹ Formaldehyde was employed as the crosslinking agent since it can be applied by a variety of techniques, since physical performance properties of the products from the various processes are different, and since treated fabrics have been well characterized.

EXPERIMENTAL

Desized, scoured, bleached 80 × 80 printcloth weighing approximately 3.5 oz./sq. yd. was crosslinked with formaldehyde by the processes which are summarized in Table I. Samples of fabric were exposed to the reagent system for varying periods to produce modified cottons having different formaldehyde contents. Sol-gel fractions in the crosslinked fabrics were determined with cupriethylenediamine hydroxide (cuene) by measurement of soluble cellulose by the method of Bullock et al.¹¹ Gel fractions, which are the differences between unity and sol fractions, were confirmed in many cases by isolation and gravimetric determination of the gel cellulose.

RESULTS AND DISCUSSION

Solubilities of cellulose and cellulose derivatives in complexing solvents such as cuprammonium hydroxide and cupriethylenediamine hydroxide (cuene) have proven to be useful in distinguishing crosslinked cellulose from unmodified cellulose or from uncrosslinked, chemically modified cellulose. The solubility-insolubility relationship in these solvents is a reliable measure of the existence of a network structure when certain criteria are satisfied: (a) the agent must be limited to a low level^{16,17} (i.e., generally below a weight gain of 10% and an apparent degree of substitution of 0.15) in order to insure that cotton chemically modified with the corresponding monofunctional substituent will be soluble and (b) the crosslinks must be stable to the strongly basic solvent in order to prevent disrup-

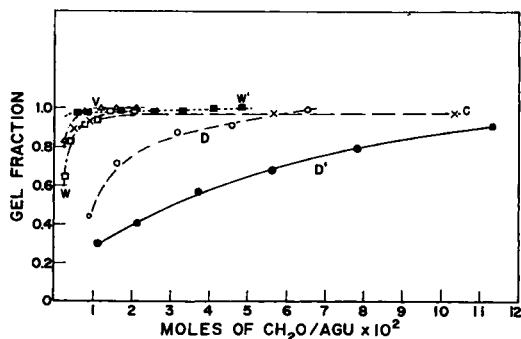


Fig. 1. Relationship of gel fraction to formaldehyde content of crosslinked cottons: (Δ) form V; (\times) form C; (\square) form W; (\blacksquare) form W'; (\circ) form D; (\bullet) form D'.

tion of crosslink by hydrolysis.¹¹ Insolubility of formaldehyde-modified cellulose in cuene is good evidence for a network structure since the mono-functional analog (i.e., cellulose methylated within the range of 0–13% methoxyl content) is soluble in cuene¹⁸ and since the formaldehyde crosslinks are stable to cuene.

The level of formaldehyde required in cotton cellulose for essentially complete development of network structure (i.e., 0.95 gel fraction) ranges from approximately 0.005 to 0.120 moles of formaldehyde per anhydroglucose unit (AGU). The variations in effectiveness of this crosslinking agent for insolubilizing cellulose molecules are evident in Figure 1. Each set of reaction conditions is characterized by a different course and efficiency of gel development. The individual processes of reaction of formaldehyde with cotton are defined and summarized in Table I. The designations which have been applied call attention to the fact that the crosslinked cottons selected for study were prepared by four different processes: form W and W' cottons resulted from reactions conducted in aqueous systems; form C cotton was prepared by a bake-cure following application of the reagent to cotton in an aqueous bath; form D and D' cottons were the result of reactions conducted in systems containing a nonaqueous (acetic acid) diluent; form V cotton was the product of a vapor-phase reaction. A major difference in the W, W' pair of cottons and in the D, D' pair is the higher concentration of formaldehyde employed in the latter member of each pair.

At gel fractions above 0.95, the formaldehyde level in the gel accounts for that of the total sample; thus there is no measurable loss in formaldehyde from the network structure during the dissolution treatment in cuene. At low gel fractions only a portion of the total formaldehyde is found in the gel. Due to difficulties in measuring formaldehyde accurately at these low levels and in small samples of gel, there is considerable uncertainty about the formaldehyde contents of the gel fractions; nevertheless, it appears that the portion of formaldehyde in the gel fraction varies, to some extent, characteristically with the conditions of reaction. The gel portion of form C cotton accounted for essentially all of the formaldehyde in all samples examined. Approximately 85% of the formaldehyde was observed to be contained in the gel fractions at the following indicated levels of moles of formaldehyde per anhydroglucose unit (AGU): form D, 0.022; form D', 0.024; form W, 0.007; form W', 0.023; and form V, 0.005.

Distributions of formaldehyde in cotton resulting from the various processes of reaction can be examined conveniently by relating moles of formaldehyde per AGU in the gel, designated $\text{CH}_2\text{O}/\text{AGU}_g$, to the number of moles of formaldehyde per AGU in the total sample, designated $\text{CH}_2\text{O}/\text{AGU}_t$. Low effectiveness of the crosslinking agent for insolubilizing all molecular units of the cellulose is indicated by a deviation from the line having a slope of unity in a plot of $\text{CH}_2\text{O}/\text{AGU}_g$ versus $\text{CH}_2\text{O}/\text{AGU}_t$ (Fig. 2). A log-log plot is employed for convenience. The more efficiently the reagent system crosslinks and insolubilizes the cotton cellulose mole-

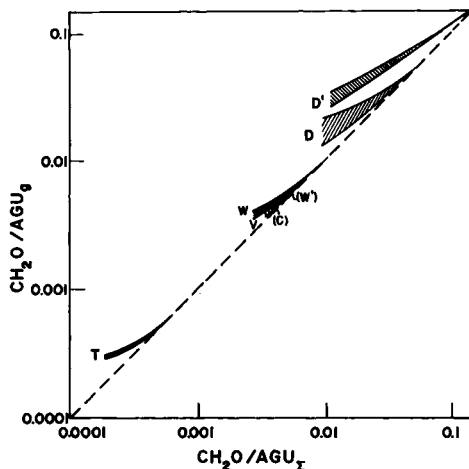


Fig. 2. Relationship of moles of formaldehyde per AGU of the gel fraction ($\text{CH}_2\text{O}/\text{AGU}_g$) to moles of formaldehyde per AGU of the total sample ($\text{CH}_2\text{O}/\text{AGU}_z$). Designations are same as those of Figure 1. *T* designates the curve calculated for crosslinking of a monodisperse cellulose in random reaction. Curves for forms C and *W'* cottons are obscured under those for forms V and *W* cottons.

cules, the closer the data will conform to the dashed line and the farther the experimental data will proceed along the dashed line from the upper right portion of the figure toward the lower left corner.

In view of uncertainties in precise formaldehyde contents in the gel fractions, data have been plotted in Figure 2, on the one extreme (upper line), on the basis that all formaldehyde is contained in the gel fraction and on the other hand, by employing the mean trend in formaldehyde content of the gel fractions from actual analyses of individual samples from each process of reaction. Since the latter are likely to err on the low side, reality is expected to lie within the crosshatched areas indicated in Figure 2.

A basis for indexing the different degrees of crosslinking is obtained by employing expressions developed by Flory^{19,20} to calculate the gel fraction and the partition of crosslinks between sol and gel for the crosslinking of an amorphous polymer (cellulose) undergoing reaction randomly.

$$-\ln W_s / (1 - W_s) = \gamma = M / M_c$$

$$\rho' = \rho(1 - W_s)$$

W_s is fraction of sol; γ is number of crosslinked units per primary molecule in the system as a whole; M is molecular weight of the sample; M_c is the molecular weight per crosslinked unit; and ρ and ρ' are crosslink densities of the total composition and the gel fraction, respectively. Curve *T* of Figure 2 is obtained from these equations for a cellulose having a degree of polymerization of 3500 (i.e., that measured by viscosity in cuene for the cotton cellulose under study²¹). Curve *T* applies, therefore, to a homogeneous crosslinking reaction for a cellulose characterized by molecules of

uniform length undergoing crosslinking at random with mono-oxymethylene units.

Deviations of actual crosslinking reactions of cotton cellulose from that calculated for the model system at 0.95 gel fraction are summarized in Table II. Crosslinking efficiencies which are listed in this table express a measure of the effectiveness of the formaldehyde in insolubilizing the cellulose molecular units. The monodisperse cellulose undergoing a homogeneous reaction to form mono-oxymethylene linkages is assigned an efficiency of unity. The extreme case of low efficiency in crosslinking the molecular units in this series of crosslinked cotton celluloses is observed for form D' cotton which requires 140 times the amount of agent calculated for network development (i.e., 0.95 gel fraction) in the model system. The reciprocal of reagent requirement provides a measure of crosslinking efficiency which increases in the order form D', form D, form C, form W, form V, form W'.

TABLE II
Crosslinking Efficiencies for Various Processes

Process	Reagent requirement 0.95 gel fraction ^a	Crosslinking efficiency ^b
Form D'	280	0.0035
Form D	120	0.008
Form C	34	0.03
Form W	24	0.04
Form V	12	0.08
Form W'	ca. 5.5 ^c	ca. 0.18 ^c

^a The relationship between the actual requirement of crosslinking agent to achieve 0.95 gel fraction under a specific set of reaction conditions and the calculated requirement of agent for crosslinking a monodisperse cellulose (DP = 3500) with mono-oxymethylene linkages in a homogeneous reaction.

^b The reciprocal of crosslink requirement for 0.95 gel fraction.

^c Based on estimate of 0.0025 mole of CH₂O per AGU at S = 0.05 from Fig. 1.

In order to obtain a more specific estimate of number of crosslinks and, especially to consider at the same time the probability of molecular degradation of the cellulose chains by hydrolysis, it is appropriate to treat the sol-gel data for these crosslinked cottons relative to another model system, for which we assume crosslinking and hydrolysis to occur at random and in proportion to the incorporation of bound formaldehyde in each specific process of reaction, i.e.,

$$q = q_0 r$$

and

$$p = p_0 r$$

where q is the proportion of AGU which crosslinked and p is the number of hydrolytic cleavages per AGU which occur as a consequence of reaction which introduces r equivalents of formaldehyde per AGU in the polymer.

Then q_0 is the density of crosslinked units and p_0 is the scission density; both are expressed per unit of reaction, r . Charlesby and Pinner²² have developed the theory and equations for the relationship of crosslink density and scission density to sol fraction S , and these authors and Valentine¹⁰ have applied them to reactions generated by irradiation. The specific equation developed for a polymer of exponential or random molecular weight distribution is utilized here.

$$S + S^{1/2} = p_0/q_0 + 2/q_0ru$$

The number of monomer units per weight average-molecule of polymer is designated u .

For random crosslinking and hydrolysis occurring in proportion to r in a polymer of random molecular weight distribution, a plot of $S + S^{1/2}$ versus $1/r$ yields a straight line with a slope $2/q_0u$ and intercept p_0/q_0 . Curves based on the experimental data from sol fractions measured on formaldehyde-crosslinked cotton celluloses are shown in Figure 3. While the experimental data generally show linear relationships for the various processes of crosslinking with formaldehyde, the form D' reaction approaches linearity only at low sol fraction, a behavior which is likely due to a contradiction of the assumption of random reaction of crosslinking reagent which is necessary for the linear relationship. Scission-crosslinking ratios, p_0/q_0 , together with other pertinent data developed from the data of Figure 3 are summarized in Table III. Values of p_0/q_0 are interestingly and surprisingly low in all cases; the higher values for the cottons from the forms C and W' processes are indications that the ratio of scission to crosslinking is more pronounced in these cases.

For a measure of the number of chemically active crosslinks introduced into cotton in each of the processes under consideration, it is informative to consider ν_e , the number (moles) of effective chain elements per gram of the network structure. Thus, ν_e , which amounts numerically to twice the number of effective crosslinks, refers to that portion of the cellulose structure extending from one crosslinkage to the next one occurring along the primary chain. To obtain values for ν_e , the proportionality constant for crosslinking, q_0 , is obtained from the slope of each curve in Figure 3. In view of the considered similarity between weight-average and viscosity-average degrees of polymerization for cellulose,^{21, 23} the value from viscosity measurements in cuene²¹ was employed ($u = 3500$). Then q_0 is substituted into an equation developed by Shultz²⁴ and simplified for the present purpose to the following:

$$\nu_e = (1 - e^{-q_0r})(1 - S^{1/2})^2m^{-1}$$

where m is the mass of the anhydroglucose unit and e is the Napierian constant.

Values of ν_e are summarized in Table III for each of the processes of crosslinking at formaldehyde contents of 0.0108 moles per AGU (0.20%), on the one hand, and at sol fractions of 0.05, on the other hand. It is

TABLE III
Parameters for Formaldehyde-Crosslinked Cottons

Crosslinked cotton	p_0/q_0^a	q_0^b	$\nu_e \times 10^5$ at 0.20% CH ₂ O	$\nu_e \times 10^5$ at $S = 0.05$
Form D'	-0.20	0.0040	c	0.36
Form D	0.05	0.0223	0.03	0.91
Form W	0.04	0.1178	0.95	0.97
Form C	0.18	0.1905	1.37	2.12
Form V	-0.07	0.1623	1.75	0.66
Form W'	0.11	0.5102	4.80 ^d	0.95 ^d

^a From intercepts of ordinate in Fig. 3.

^b From slope = $2/q_0u$ in Fig. 3; $u = 3500$.

^c Inapplicable in this range due to nonlinearity.

^d Based on estimate of 0.0025 moles of CH₂O per anhydroglucose unit at $S = 0.05$.

evident that the number of effective chain elements or number of effective crosslinks per gram at the 0.0108 level of formaldehyde decrease in the order W', V, C, W, D, and D'.

At sol fractions of 0.05 in the various crosslinked cottons, the values of ν_e are essentially identical for forms D, W, and W' cottons. Form D' shows the lowest number of effective chain elements and form C, the largest number. When the different amounts of formaldehyde which were required to attain this sol (or gel) fraction in the various cottons are taken into consideration, the relative order of moles of formaldehyde per effective chain element (i.e., CH₂O/ ν_e) is found to be: form D', 210; form D, 37; form W, 6.7; form V, 5.1; form C, 4.3; and form W', 1.6. This order of increasing effectiveness of utilization of formaldehyde in the development of effective crosslinks is similar to the order of increasing ν_e at the 0.20% level of formaldehyde (Table III) and to the order of increasing efficiencies of crosslinking (Table II). Only the position of form C cotton changes in these relative sequences. It is most significant at this stage of the analysis for crosslinks that substantial differences in numbers of effective chain elements or in crosslinking efficiencies are obtained for the crosslinked cottons and that the orders observed are consistent (excepting form C) from two different mathematical analysis and at two levels of analysis ($S = 0.05$, and CH₂O = 0.20%).

CONCLUSIONS

Sol-gel data on formaldehyde-crosslinked cotton celluloses, which were prepared under different conditions of reaction, provide a measure of the efficiency with which the crosslinking agent is utilized for insolubilizing the molecular units of the cellulose (Table II). Relatively low efficiency of utilization of crosslinking agent is indicated for all processes, but especially for the forms D' and D processes. The apparent efficiency of crosslinking from the highest (form W') to the lowest (form D') in this series differs by a factor of approximately 40.

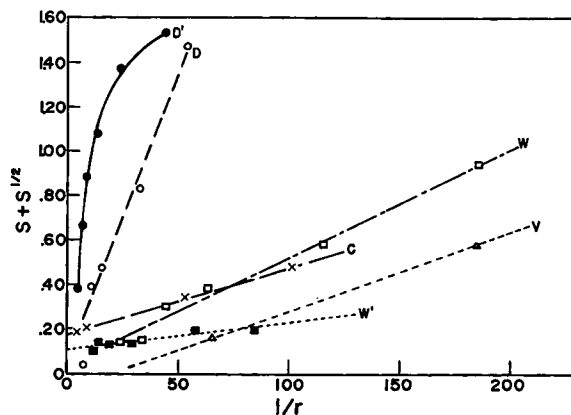


Fig. 3. Curves of $S + S^{1/2}$ against $1/r$. Designations are the same as those of Figure 1.

Interpretation of the sol-gel data by means of equations developed by Charlesby and Pinner and by Schultz leads to values of number (moles) of effective chain elements per gram, ν_e , which provide a basis for relative comparison of the crosslink densities developed in the different formaldehyde-modified cottons at a specific level of incorporated agent and also at essentially complete gel formation (Table III). The numbers of effective chain elements or crosslinks per gram in these crosslinked cottons at the level of 0.0108 moles of formaldehyde per AGU decrease over two orders of magnitude in the following sequence: form $W' > \text{form } V > \text{form } C > \text{form } W > \text{form } D > \text{form } D'$.

While conditions of reaction for introduction of formaldehyde into cotton have been selected for each of the individual processes so that forms D, V, C, and W processes are illustrative and somewhat representative of each type of reaction, it is important to note that conditions of reaction for each of these processes may be altered over a wide range with corresponding effect upon the characteristics of the product.

It must be emphasized that the interpretation of the sol-gel data has been made relative to models assuming random reaction of crosslinking reagent with the polymer substrate. The gross deviation of data for form D' cotton from the linearity expected for random reaction (Fig. 3) suggests a nonrandom reaction and substantial heterogeneity of distribution of crosslinks in this case. It is tempting to think that the linearity of the $S + S^{1/2}$ versus $1/r$ relationships for the other crosslinked cottons suggests an apparent randomness of reaction that is hardly expected on the basis of the semicrystalline nature of the cotton and the heterogeneous nature of the reaction. In any case, a high degree of accessibility of reagent to all molecular units of the cellulose is indicated for forms W' , V, C, and W cottons, and especially form W' cotton.

The authors wish to acknowledge the analytical assistance of John S. Mason and the preparation of line drawings by George I. Pittman.

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Résumé

On a mesuré les fractions relatives sol-gel pour la cellulose de coton pontée avec du formaldéhyde dans des conditions de réaction très différentes; on en déduit l'efficacité de pontage dans les divers processus. L'utilisation du formaldéhyde la plus efficace pour insolubiliser les chaînes moléculaires est obtenue au cours d'un procédé aqueux (forme W') l'utilisation la moins efficace a lieu dans un procédé non-aqueux (forme D'), la différence; d'efficacité s'élevant approximativement à un facteur égal à 40. L'interprétation des résultats sol-gel a été faite par comparaison avec un modèle qui postule une réaction statistique de l'agent de pontage à travers la cellulose de coton et au moyen des relations indiquées par Charlesby et Pinner et par Shultz. Ceci permet l'estimation des nombres relatifs (moles) des éléments de chaîne effectifs par gramme, ν_e (c.à.d. deux fois le nombre de ponts); ils décroissent dans l'ordre suivant pour des cotons contenant 0.2% de formaldéhyde (c.à.d. 6.7×10^{-5} moles/g); le procédé aqueux, une concentration en formaldéhyde plus élevée (W', $\nu_e = 4.8 \times 10^{-5}$); le procédé vapeur (V, $\nu_e = 1.75 \times 10^{-5}$), le procédé par cuisson (C, $\nu_e = 1.37 \times 10^{-5}$), le procédé aqueux à concentration en formaldéhyde plus faible (W, $\nu_e = 0.95 \times 10^{-5}$), le procédé non-aqueux (D, $\nu_e = 0.03 \times 10^{-5}$).

Zusammenfassung

Sol-Gelanteile wurden an mit Formaldehyd unter sehr verschiedenartigen Reaktionsbedingungen vernetzten Baumwollcellulosen gemessen und zur Bestimmung der Vernetzungsausbeute bei den verschiedenen Prozessen verwendet. Die wirksamste Verwendung des Formaldehyds zur Insolubilisierung der Molekülketten wird bei einem Prozess in Wasserphase (Form W' erreicht) und die am wenigsten wirksame bei einem nicht-wässrigen Prozess (Form D'), wobei sich die Ausbeute um etwa einen Faktor 40 unterscheidet. Die Auswertung der Sol-Geldaten erfolgte nach einem Modell mit Annahme statistischer Reaktion des Vernetzungsmittels in der gesamten Cellulose und mit den von Charlesby und Pinner sowie von Shultz entwickelten Beziehungen. Damit werden relative Molzahlen effektiver Kettenelemente pro Gramm ν_e (d.i. die doppelte Zahl effektiver Vernetzungsstellen) erhalten, welche bei Baumwolle mit 0,20% Formaldehyd (d.i. $6,7 \times 10^{-5}$ Mol/g) in folgender Reihenfolge abnehmen: Wasserprozess, höhere Formaldehydkonzentration (W', $\nu_e = 4,8 \times 10^{-5}$); Dampfphasprozess (V, $\nu_e = 1,75 \times 10^{-5}$); Backhärtungsprozess (C, $\nu_e = 1,37 \times 10^{-5}$); Wasserprozess, niedrigere Formaldehydkonzentration (W, $\nu_e = 0,95 \times 10^{-5}$); nicht-wässriger Prozess (D, $\nu_e = 0,03 \times 10^{-5}$).

Received May 2, 1966

Prod. No. 1415