



SURAT KETERANGAN
MELAKUKAN KEGIATAN PENGABDIAN KEPADA MASYARAKAT
INSTITUT TEKNOLOGI NASIONAL
No. 539/C.02.01/LP2M/VIII/2018

Yang bertanda tangan di bawah ini,

Nama : Dr. Tarsisius Kristyadi, S.T., M.T.
Jabatan : Kepala
Unit Kerja : LP2M-Itenas
Jl. P.K.H. Mustafa No.23 Bandung

Menerangkan bahwa,

Nama	NPP	Jabatan
Dicky Dermawan, S.T., M.T.	960603	Technical Advisor

Telah melakukan kegiatan Pengabdian kepada Masyarakat sebagai berikut :

Nama Kegiatan : Pengembangan Produk Resain Adhesive
Tempat : PT. Dover Chemical
Waktu : 24 - 27 Juli 2018
Sumber Dana : PT. Dover Chemical

Demikian surat keterangan ini dibuat untuk dapat dipergunakan sebagaimana mestinya.

Bandung, 07 Agustus 2018

Lembaga Penelitian dan Pengabdian
kepada Masyarakat (LP2M) Itenas
Kepala,

Dr. Tarsisius Kristyadi, S.T., M.T.
NPP 960604

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SURAT KETERANGAN

Yang bertanda tangan di bawah ini,

Nama : Dr. H. Dade Suparna, SH.,MH
Jabatan : HR & GA Manager
Alamat : Jl. Raya Merak KM.117 Ds. Gerem, Kec. Grogol
Kota Cilegon – Banten 42438

Menerangkan bahwa :

Nama : Dicky Dermawan
Jabatan : Dosen Program Studi Teknik Kimia Itenas
Alamat : Jl. PHH. Mustafa 23 Bandung 40124

Telah melakukan kegiatan sebagai Technical Advisor pada :

Judul : Studi Pengembangan Produk Resin Adhesive untuk Industri Panel Kayu
Tempat : Production & Development Unit PT. Dover Chemical
Jl. Raya Merak KM.117 Ds. Gerem, Grogol, Kota Cilegon Banten 42438
Waktu : 24 – 26 Juli 2018

Berdasarkan Nota Kesepahaman antara Jurusan Teknik Kimia Institut Teknologi Nasional (Itenas) dengan PT. Dover Chemical tanggal tiga puluh bulan Januari tahun dua ribu tujuh belas.

Demikian surat keterangan ini dibuat untuk dapat digunakan sebagaimana mestinya.

Cilegon, 26 Juli 2018


P.T. Dover Chemical

Dr. H. Dade Suparna, SH.,MH
HR & GA Manager



THE DOVECHEM GROUP





SURAT TUGAS
No. 460/J.16.01/LP2M/VII/2018

Yang bertanda tangan dibawah ini,

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Menerangkan bahwa :

Nama	NPP	Jabatan
Dicky Dermawan, S.T., M.T.	960603	Dosen

Ditugaskan untuk melakukan,

Kegiatan : Pengembangan Produk Resain Adhesive
Sebagai : Technical Advisor
Tempat : PT. Dover Chemical
Jalan Raya Merak Km. 117 Cilegon, Banten
Hari/Tanggal : Selasa-Kamis/24-26 Juli 2018

Demikian surat tugas ini dibuat untuk dipergunakan sebagaimana mestinya.

Bandung, 16 Juli 2018

Lembaga Penelitian dan Pengabdian
kepada Masyarakat (LP2M) Itenas
Kepala,

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NPP. 960604

Tembusan Yth :

1. Dekan FTI
2. KaJur Teknik Kimia
3. Kepala Kepegawaian

Urea – Formaldehyde Reaction Chemistry

Dicky Dermawan
Chemical Engineering Department
Institut Teknologi Nasional
Bandung
2018

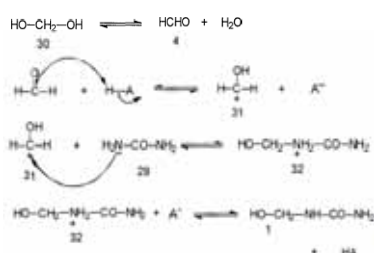
Outline

Methylation
Condensation
Effect of Process Variables:
Molar Ratio
Temperature
pH
Number of Condensation Steps

Urea – Formaldehyde Reactions: 1-Monomethylol Urea

This reaction is **reversible** in neutral, acidic and basic solutions. The forward reaction is bimolecular and the reverse reaction is monomolecular, and both the forward and reverse processes are catalysed by hydrogen ions or hydroxide ions.

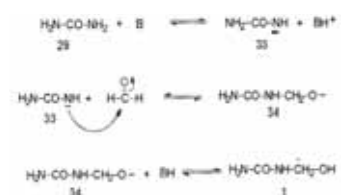
Mechanism for acid catalyzed reaction:



Urea – Formaldehyde Reactions: Monomethylol Urea

This reaction is **reversible** in neutral, acidic and basic solutions. The forward reaction is bimolecular and the reverse reaction is monomolecular, and both the forward and reverse processes are catalysed by hydrogen ions or hydroxide ions.

Mechanism for base catalyzed reaction:

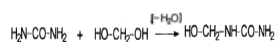


Urea – Formaldehyde Reactions: Monomethylol Urea

This reaction is **reversible** in neutral, acidic and basic solutions. The forward reaction is bimolecular and the reverse reaction is monomolecular, and both the forward and reverse processes are catalysed by hydrogen ions or hydroxide ions.

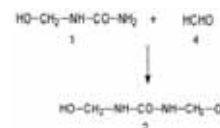
Alternative mechanism:

The formation of methylene glycol in aqueous solution, however, has prompted the suggestion that the condensation involves a direct displacement reaction between urea and methylene glycol



Urea – Formaldehyde Reactions: 2-Dimethylol Urea

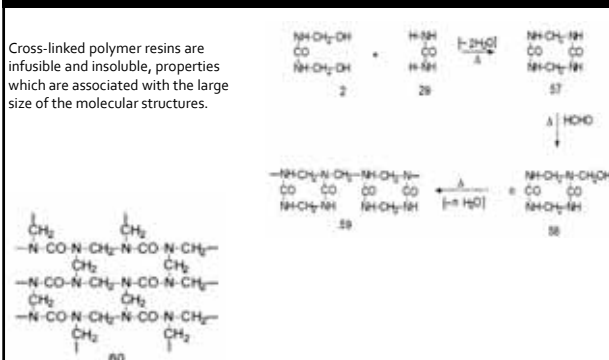
Under the same conditions required for the formation of monomethylolurea 1, but using a 2 molar excess of formaldehyde 4, monomethylolurea 1 and formaldehyde 4 react to give dimethylolurea 2. The rates of both the forward reaction and the reverse reaction were found to be proportional to the hydrogen ion concentration.



The mechanism is considered to be similar to that for the formation of monomethylolurea under both acidic and basic conditions.

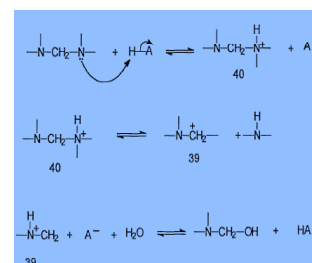
Urea – Formaldehyde Reactions: Polymer Formation

Cross-linked polymer resins are infusible and insoluble, properties which are associated with the large size of the molecular structures.



Urea – Formaldehyde Reactions: Acid-catalyzed Hydrolysis

In acidic conditions (pH = 3-5), methylenediurea derivatives can be hydrolysed to urea and monomethylolurea derivatives, while the hydrolysis of dimethyldiurea 2 is a reversible process, with the rates of both the forward and reverse reactions being directly proportional to the hydrogen ion concentration.



Variables affecting U – F Reactions

Reactions conducted at lower temperatures take longer to reach the required viscosity; under these conditions, different reactions may take place, affording different components and, thus, resins with different properties.

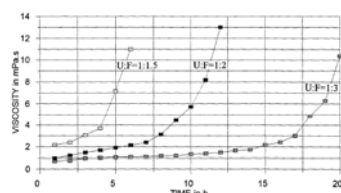
In fact, five parameters:

1. the U:F molar ratio
2. the pH
3. the duration of the reaction
4. the reaction temperature
5. the nature of the catalyst

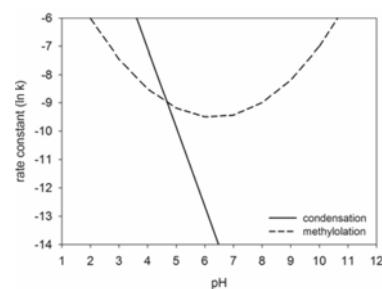
have all been found to affect the average structure and properties of urea-formaldehyde resins, and resins with particular properties can be produced by varying these parameters.

Effect of Molar Ratio

Comparative plots of viscosity against time for reactions at 80°C & pH = 5 showed that increasing F/U ratio will slowing down the reaction.



Effect of Reaction pH



Effect of Reaction pH

Different types of UF dimers will be formed at different pH values. The dimers formed will have an impact on the properties of the finished adhesive, e.g. the formaldehyde emissions can be controlled by controlling the composition of dimers.

UF dimers with methylene linkages are formed if the pH during condensation is kept at 8 or less. Additionally, it was also shown that methylene linkages are favored by a decrease in pH. [The formation of UF dimers with ether linkages had a minimum yield point at pH 8.](#) At either side of that value, independently of if the pH value is increased or decreased, the formation of ether linkages increased.

At pH 6.5-7.5, both of the substances containing methylene linkages and ether linkages were formed to the same extent.

At pH 6 or less, however, ether linkages were formed in the favor of methylene linkages. This was explained by that the methylation of the urea was slower than at higher pH values. As a consequence, unsubstituted amino groups will remain to a larger extent, which favors the formation of methylene linkages.

Effect of Reaction Temperature

Secara umum makin tinggi suhu reaksi makin cepat lah....

The effect of the reaction temperature has on the synthesis [is dependent on the pH value of the reaction mixture](#), where these temperature alternations occur. Temperature variations were studied at both pH 7.0 and 8.5. The temperatures chosen were 60, 70 and 80°C.

The temperature had no impact on the substitution reaction between urea and formaldehyde at pH 8.5, but an increase in amount of substituted urea was observed at pH 7. The amount of condensed di- and triureas was also increased with temperature; however the rate of hydrolysis was also increased with temperature.

The most pronounced effect of the reaction temperature was displayed at pH 7. At pH 7 the amount of substances larger than diureas, were increased from 9% to 55% by increasing the temperature from 60 to 80°C.

Effect of Catalyst Type

Not solely depending on reaction pH, the type of acid and base used results in different product properties.

Effect of Number of Urea Addition Step

The number of condensation steps and the duration of these has an effect on the molecular structure of the resin, and thus also upon its inherent properties, such as molecular weight. [When urea is added, it will break some of the bonds already formed between different UF monomers.](#) The urea will then react with the newly released formaldehyde to form methylol ureas. As the number of urea steps is increased, more urea will be added that breaks up the larger structures and, as a consequence, the reaction mixture becomes more homogenous. This means that if the number of condensation steps is increased, the polydispersity index (PDI) is decreased.

PDI is an important factor when considering adhesives. This is due to that different sizes of molecules have different roles to play when it comes to the adhesive property of the resin. Smaller molecules are better at wetting the surface enables a good adhesion. The larger molecules, on the other hand, have the ability to form entanglements with other polymeric chains. These entanglements ensure that the cohesion is strong enough for the adhesive molecules to hold together. Cohesion is the ability for identical or similar molecules to hold together, adhesion is the ability for different molecules to hold together. By combining good cohesive and adhesive properties an adhesive can adhere well to the two substrate surfaces, and at the same time have sufficient strength within the glue line. [A sufficiently high PDI would, therefore, ensure a good combination between adhesive and cohesive ability, which in turn ensures good adhesion.](#)

Effect of Number of Urea Addition Step

Formaldehyde emissions are also affected by the number and duration of condensations steps. [The emissions of formaldehyde were lower with increasing number of condensation steps](#), and increasing duration for which they took place.

The decrease in formaldehyde emissions as a consequence of an increase in condensation steps might be explained by that when the numbers of condensations were increased, the F/U molar ratio decreased in each step. This means that the number of methylol groups added per urea molecule would be fewer and fewer for each step. The added urea would also break apart the larger structure. The methylol groups on these structures as well as on the newly formed methylol ureas would then have a greater chance of reacting with an amino group instead of another methylol group. Consequently, this will generate more methyl linkages and fewer ether linkages which might result in lower formaldehyde emissions.

Effect of Final F/U Molar Ratio in Typical Alkaline – Acid Process

Functional Group	Resonance Position (ppm)	Amount of Each Group as a Percentage of Total Formaldehyde		
		*Resin: A	B	C
—NH—CH ₂ OH	64.8	44.1	50.6	36.6
—N(CH ₂ OH) ₂	71.6	14.0	10.4	13.4
—NH—CH ₂ —O—CH ₂ —NH—	69.6	15.6	13.7	17.1
—NH—CH ₂ —O—CH ₂ OH				
—N(CH ₂)—CH ₂ —O—CH ₂ —NH—	76.2	7.8	5.7	9.6
—N(CH ₂)—CH ₂ —O—CH ₂ OH				
—NH—CH ₂ —NH—	47.2	8.3	8.1	6.6
—N(CH ₂)—CH ₂ —NH—	53.3	10.1	10.7	11.5
HO—CH ₂ —OH	82.9	0.0	1.0	5.1
HOCH ₂ —O—CH ₂ OH	86.3	0.0	0.0	0.0
HOCH ₂ —O—CH ₂ —O—CH ₂ OH	86.8	0.0	0.0	0.0

*Resin description

A—1.1 MR (standard cook)

B—1.43 MR

C—2.0 MR

Ether formation

Free formaldehyde

Linear vs branching

Effect of FFA Molar Ratio at Condensation Step in Typical Alkaline – Acid Process (Final molar ratio = 2.2)

Functional Group	Resonance Position (ppm)	*Resin:	Amount of Each Group as a Percentage of Total Formaldehyde		
			A	B	C
—NH—CH ₂ OH	64.8		65.2	44.1	31.7
—N(CH ₂ OH) ₂	71.6		5.4	14.0	10.7
—NH—CH ₂ —O—CH ₂ —NH—	69.6		13.8	15.6	20.4
—NH—CH ₂ —O—CH ₂ OH					
—N(CH ₂ —)CH ₂ —O—CH ₂ —NH—	76.2		0.0	7.8	8.2
—N(CH ₂ —)CH ₂ —O—CH ₂ OH					
—NH—CH ₂ —NH—	47.2		10.9	8.3	19.2
—N(CH ₂ —)CH ₂ —NH—	53.5		4.6	10.1	9.6
HO—CH ₂ —OH	82.9		0.0	0.0	0.0
HOCH ₂ —O—CH ₂ OH	86.1		0.0	0.0	0.0
HOCH ₂ —O—CH ₂ —O—CH ₂ OH	86.8		0.0	0.0	0.0

*Resin description

A—acid advance begun at 3.0 MR

B—acid advance done at 2.2 MR (standard cook)

C—acid advance done at 1.1 MR

Rate of reaction
Linear vs branching

Effect of Reaction pH at Methylation Step in Typical Alkaline – Acid Process

Functional Group	Resonance Position (ppm)	*Resin:	Amount of Each Group as a Percentage of Total Formaldehyde	
			A	B
—NH—CH ₂ OH	64.8		24.1	31.7
—N(CH ₂ OH) ₂	71.6		2.2	10.7
—NH—CH ₂ —O—CH ₂ —NH—	69.6		4.3	20.4
—NH—CH ₂ —O—CH ₂ OH				
—N(CH ₂ —)CH ₂ —O—CH ₂ —NH—	76.2		0.0	8.2
—N(CH ₂ —)CH ₂ —O—CH ₂ OH				
—NH—CH ₂ —NH—	47.2		29.3	19.2
—N(CH ₂ —)CH ₂ —NH—	53.5		12.0	9.6
HO—CH ₂ —OH	82.9		0.0	0.0
HOCH ₂ —O—CH ₂ OH	86.1		0.0	0.0
HOCH ₂ —O—CH ₂ —O—CH ₂ OH	86.8		0.0	0.0
—NH—CO—NH—	74.8		11.1	0.0
—CH ₂ —O—CH ₂ —				
—NH—CO—N—CH ₂ OH	(1) 68.6		5.3	0.0
—CH ₂ —O—CH ₂ —	(1) 78.9		8.9	0.0
—CH ₂ —O—CH ₂ —	(2) 78.9		8.9	0.0

*Resin description

A—modified alkaline treatment (higher pH and longer time)

B—standard alkaline treatment

(both resins were advanced at 1.1 MR)

No ether at too high pH, possibly cause by hydrolysis at acid condensation step

Uron at high pH

More methanol at higher pH due to Cannizzaro reaction

Effect of Condensation Time in Typical Alkaline – Acid Process

Functional Group	Resonance Position (ppm)	*Resin:	Amount of Each Group as a Percentage of Total Formaldehyde	
			A	B
—NH—CH ₂ OH	64.8		44.1	35.2
—N(CH ₂ OH) ₂	71.6		14.0	11.4
—NH—CH ₂ —O—CH ₂ —NH—	69.6		15.6	9.9
—NH—CH ₂ —O—CH ₂ OH				
—N(CH ₂ —)CH ₂ —O—CH ₂ —NH—	76.2		7.8	5.9
—N(CH ₂ —)CH ₂ —O—CH ₂ OH				
—NH—CH ₂ —NH—	47.2		8.3	15.7
—N(CH ₂ —)CH ₂ —NH—	53.5		10.1	22.0
HO—CH ₂ —OH	82.9		0.0	0.0
HOCH ₂ —O—CH ₂ OH	86.1		0.0	0.0
HOCH ₂ —O—CH ₂ —O—CH ₂ OH	86.8		0.0	0.0

*Resin description

A—standard cook (final viscosity—270 cps)

B—high extent of reaction (final viscosity—715 cps)

Less ether at longer duration due to hydrolysis

Higher MW polymer

Higher viscosity product

Effect of Concentration in Typical Alkaline – Acid Process

Functional Group	Resonance Position (ppm)	*Resin:	Amount of Each Group as a Percentage of Total Formaldehyde	
			A	B
—NH—CH ₂ OH	64.8		44.1	35.2
—N(CH ₂ OH) ₂	71.6		14.0	5.1
—NH—CH ₂ —O—CH ₂ —NH—	69.6		15.6	4.3
—NH—CH ₂ —O—CH ₂ OH				
—N(CH ₂ —)CH ₂ —O—CH ₂ —NH—	76.2		7.8	0.0
—N(CH ₂ —)CH ₂ —O—CH ₂ OH				
—NH—CH ₂ —NH—	47.2		8.3	2.8
—N(CH ₂ —)CH ₂ —NH—	53.5		10.1	0.0
HO—CH ₂ —OH	82.9		0.0	1.2
HOCH ₂ —O—CH ₂ OH	86.1		0.0	0.0
HOCH ₂ —O—CH ₂ —O—CH ₂ OH	86.8		0.0	0.0
—NH—CO—NH—	75.0		0.0	0.6
—CH ₂ —O—CH ₂ —				
—NH—CO—N—CH ₂ OH	(1) 68.4		0.0	1.0
—CH ₂ —O—CH ₂ —	(1) 78.8		0.0	1.2
—CH ₂ —O—CH ₂ —	(2) 78.8		0.0	1.2

*Resin description

A—standard cook (cooked at 65% solids)

B—dilute cook (cooked at 3% solids and condensed to 30% by vacuum distillation)

Slower reaction at dilute concentration

Less ether linkage at dilute concentration

Uron formation at dilute concentration