

CYLINK[®] NBMA Monomer

N-Butoxymethyl Acrylamide for Non-Wovens and Other Applications

Introduction

N-butoxymethyl acrylamide (NBMA), a homolog of N-methylolacrylamide (NMA), is the n-butyl ether of NMA. It contains a readily polymerizable vinyl group as well as a crosslinkable n-butoxymethyl group. The n-butyl group imparts organic solubility to NBMA permitting the preparation of three general classes of polymers:

1. Organic soluble or solvent based polymers which, on application can be thermoset or crosslinked through either self or external crosslinking mechanisms.
2. Water based or emulsion polymers which, can also be either self or externally crosslinked at the point of application.

The presence of the N-butoxymethyl group offers several advantages in emulsion polymers.

- The organic solubility of NBMA enhances its compatibility with other vinyl monomers permitting the incorporation of larger quantities into the polymer backbone relative to NMA.
- The alkyl ether stabilizes the methylol group, thus providing greater resistance to premature crosslinking.
- The N-butoxymethyl group in NBMA provides a more controllable cure rate, thus minimizing cracking and checking of the final thermoset polymers.

3. In radiation curing systems, NBMA can be used as a reactive diluent. All of the components present in NBMA with the exception of a small amount of n-butanol are radiation polymerizable through the vinyl double bond. Upon further heating of the NBMA-containing radiation-cured polymer, additional crosslinking can take place through the N-butoxymethyl group.

The major polymer properties imparted by NBMA include:

- Improved water and solvent resistance
- Improved adhesion
- Improved tensile strength
- Flexibility
- Resistance to blocking
- Good hand properties

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CAS No. 1852-16-0

Typical Properties

Physical Properties

Appearance

NBMA 801 NBMA 501

Clear to slightly hazy liquid;
colorless to pale yellow
in color.

Assay

Active, %
N-Methylolacrylamide, %
Acrylamide, %
n-Butanol, %
Inhibitor, MEHQ, ppm
Formaldehyde, max., %
Viscosity, cps, @ 25°C
Brookfield LVT,
No. 1 spindle, 60 rpm
Refractive Index, n_D^{25}
Specific gravity, @ 25°C
Homo polymer T_g , °C

82 min.	51 min.
4.0 max.	3.0 max.
6.0 max.	4.0 max.
5.0 max.	4.0 max.
450	350
0.5 max.	0.5 max.
80 max.	80 max.
1.430 - 1.440	
0.95	0.91
0	0

Solubility, @ 25°C

Water	Insoluble
Acetone	Soluble
Acetonitrile	Soluble
Benzene	Soluble
Carbon tetrachloride	Soluble
Chloroform	Soluble
Dimethylformamide	Soluble
Ethyl acetate	Soluble
Hexane	Insoluble
Methanol	Soluble
Tetrahydrofuran	Soluble
Acrylonitrile	Soluble
Ethyl acrylate	Soluble
Methyl methacrylate	Soluble
Styrene	Soluble
Vinyl acetate	Soluble

Chemical Reactions and Properties

Reactions of the Vinyl Group

NBMA copolymerizes readily with most vinyl monomers such as acrylates, styrene, vinyl chloride, acrylonitrile, acrylamide and vinyl acetate.

Reaction of the N-Butoxymethyl Group

Copolymers made with NBMA can be crosslinked utilizing the reactivity of the N-butoxymethyl group. The cross-linking reaction can occur via condensation reaction of the N-butoxymethyl groups with hydroxyl, carboxyl, amine or amide groups that may be present in the copolymer system or in the substrates (e.g. cellulosic products) to which the NBMA-containing copolymer is applied. While heat alone can affect post cure (cross-linking), generally a combination of acid catalyst and one or more of the above mentioned groups in the polymer reduces the time and temperature of cure. Such groups will also tie up the hydroxymethyl group as part of the polymer or as part of the polymer-to-substrate linkage.

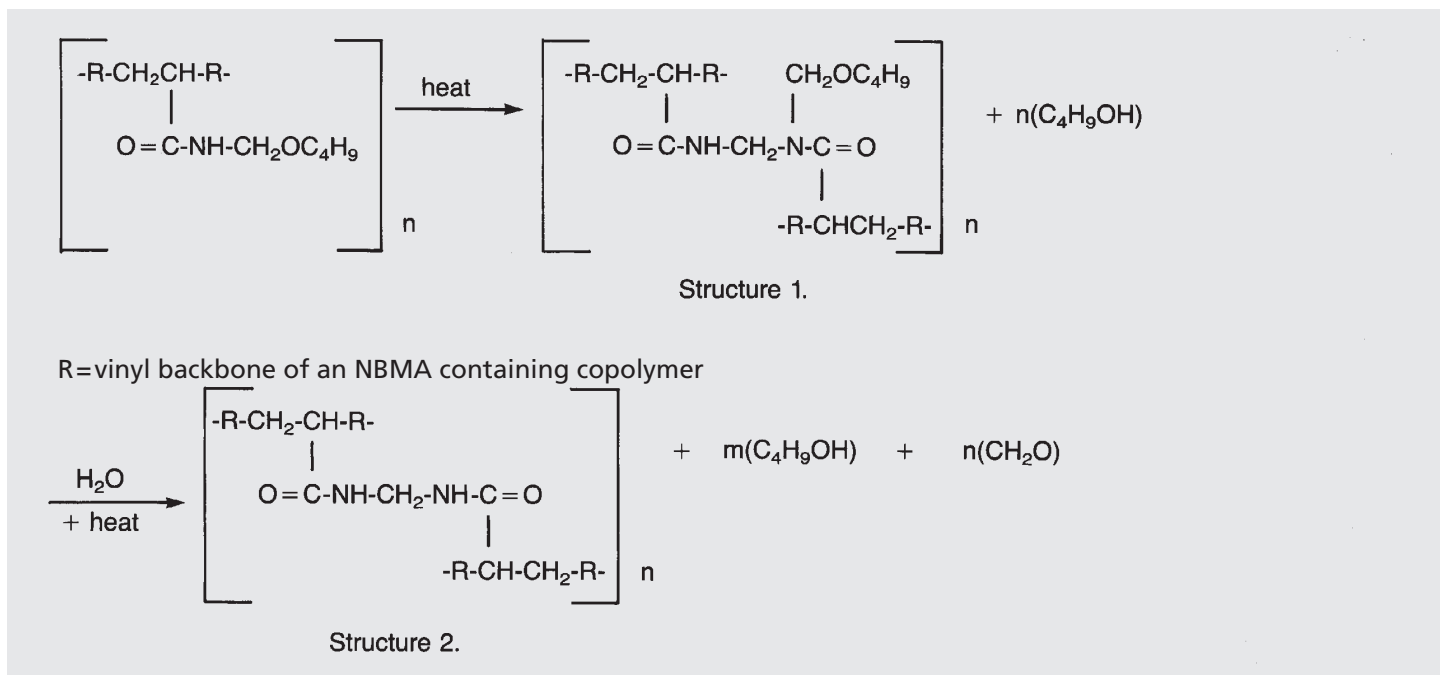
The crosslinking (cure) mechanism of the N-butoxymethyl moiety in such polymers or in polymer-to-substrate linkages is obviously a very complex chemical reaction that can only be depicted in a general way by chemical equations. n-butanol is usually generated during the crosslinking reaction.

Stability

NBMA is stable under normal storage conditions. However, exposure to ultraviolet light, low pH and/or unnecessary heat should be avoided. Storage in a cool dark place is recommended. Contact with metallic copper, bronze or brass during storage should be avoided.

These reactions can be illustrated generally by chemical equations as follows:

Curing by Heat



In the first step, thermal condensation yields the alcohol as the only cleavage product, yielding Structure 1.

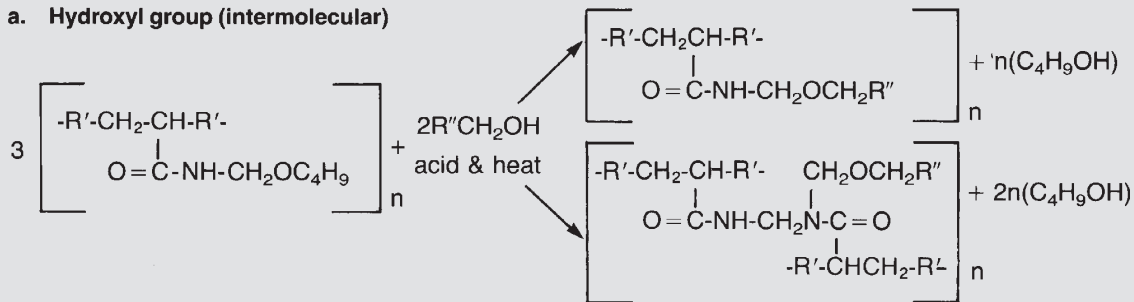
This intermediate can be hydrolyzed in the presence of water and heat to yield Structure 2, n-butyl alcohol and formaldehyde.

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Crosslinking with Hydroxyl Groups

The use of an acid catalyst in the presence of a hydroxyl containing compound minimizes or eliminates the release of formaldehyde.

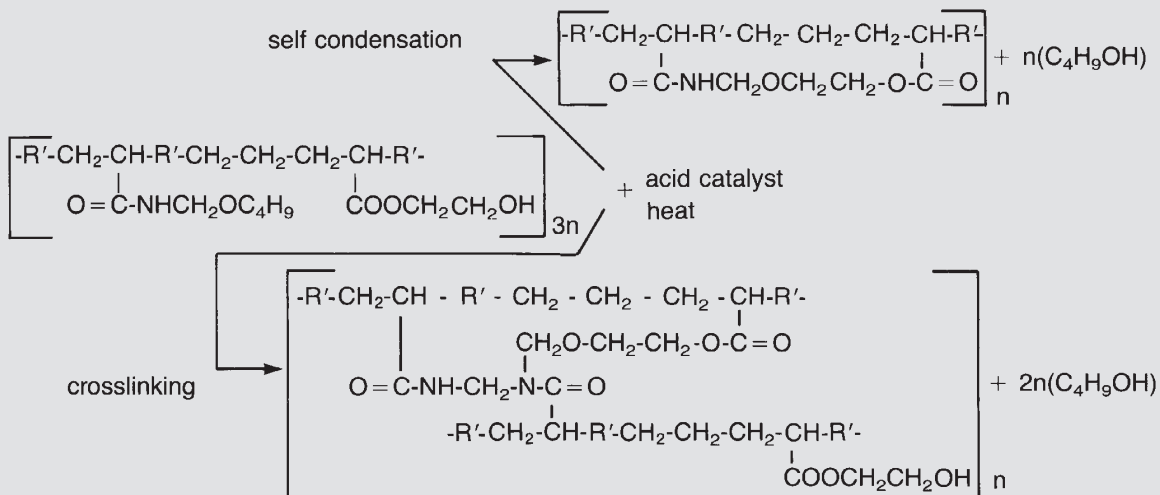
a. Hydroxyl group (intermolecular)



R' = vinyl polymer backbone

R'' = polymer or substrate containing hydroxyl groups

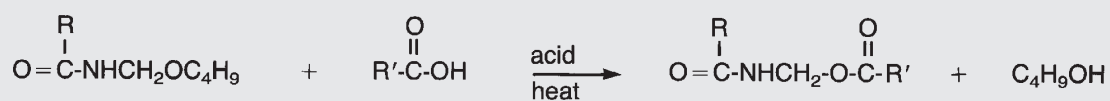
b. Hydroxyl group (intramolecular)



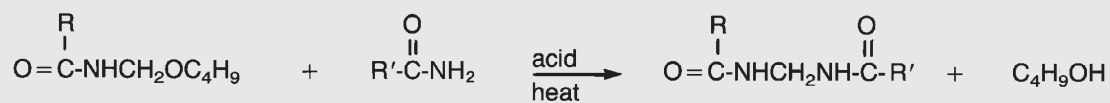
Reaction with Carboxyl and Amine Groups

Reaction with these groups follows the same pattern of crosslinking shown for the hydroxyl group. These reactions are depicted below showing only the reactive groups of the polymer backbone.

Carboxyl group



Amine group



R = polymer R' = polymer

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Polymerization: Recipes, Procedures and Properties for Non-Woven Applications

NBMA can be readily copolymerized with most monomers by either solution or emulsion polymerization. Much work has been done with this monomer and many examples are available from the literature, including application test data related to the use of the resulting polymers.

POLYMERIZATION OF BUTYLACRYLATE - METHYLMETHACRYLATE- N-BUTOXYMETHYL ACRYLAMIDE TERPOLYMER

Solids: 51% **SAA level:** AEROSOL® 501 surfactant- 2.7 phm **SAA level:** AEROSOL 103 surfactant- 0.6 phm

Ratio: BA/MMA/MAA/NBMA = 46.6/49.7/0.6/4

I. RECIPE: 245A

A) Kettle charge: **parts per weight**

DI Water	260.0
AEROSOL 501 surfactant (50%)	6.0
BA	21.0
MMA	26.2

Initial Catalyst

DI Water	30.0
KPS	0.8

B) Monomer charge:

DI Water	100.0
AEROSOL 501 surfactant (50%)	20.0
AEROSOL A103 surfactant (34%)	8.0
BA	210.0
MMA	220.0
MAA	3.0
NBMA 801- 80%	24.4

C) Catalyst charge:

DI Water	60.0
KP	0.8

II. Glass Transition Temperature:

T_g is calculated as - 12.2°C.

III. Procedure:

A) Preparation of kettle charge:

Dissolve 6.0 parts AEROSOL 501 surfactant in 260 parts deionized water. Purge with nitrogen and heat to 65°C.

Mix 26.2 parts methylmethacrylate and 21 parts butylacrylate and add into kettle. Slow down the nitrogen purge and wait for temperature to requilibrate.

Dissolve 0.8 parts of KPS in 30 parts of Deionized water and place aside with name initial catalyst.

B) Preparation of monomer charge:

Dissolve 20 parts AEROSOL 501 surfactant and 8 parts AEROSOL A103 surfactant in 100 parts deionized water. Add to this solution under sufficient stirring a mix of 210 parts butylacrylate, 220 parts methylmethacrylate, 3 parts of methacrylic acid and 24.4 parts 80% n-butoxymethylacrylamide-801. This pre-emulsion is placed in an addition vessel under continuous stirring.

C) Preparation of catalyst charge:

Dissolve 0.8 parts potassiumpersulphate in 60 parts deionized water and place in an addition vessel.

D) Preparation of latex:

When the contents of the polymerization kettle reach 65°C, add the initial catalyst while raising the temperature to 75°C. After initiation start addition of the pre-emulsion and catalyst at a rate of 2.4 and 0.2 parts per minute resp. Total addition time should require 4 hours. After finishing the addition hold at 75°C for another 1 hour to complete the reaction and cool to room temperature. Neutralize the polymer to 8.5 pH with 30 % ammonium hydroxide and filter.

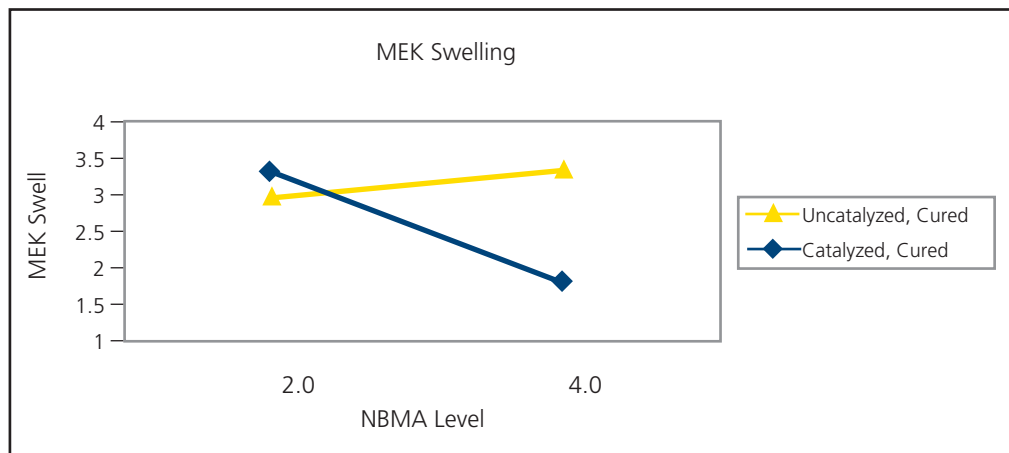
IV. Results:

Parameter	Poly(BA/MMA/MAA/NBMA-2)	Poly(BA/MMA/MAA/NBMA-4)
Solids (%)	50.1	50.3
pH	8.5	8.4
PS (nm)	176	176
Viscosity (#1, 60RPM)	48.0	63.2
Grit 100# (%)	0.15	0.07
Reactor coat (%)	0.3	0.9
Gel Content (%)	10.5	11.2

V. Film Characteristics:

MEK Swelling @ 130°C,
5 minutes

	Poly(BA/MMA/MAA/NBMA-2)	Poly(BA/MMA/MAA/NBMA-4)
Uncatalyzed	3.05	3.40
Catalyzed, pH-3	3.38	1.97



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POLYMERIZATION OF VINYL ACETATE - BUTYL ACRYLATE - N-BUTOXYMETHYL ACRYLAMIDE -TERPOLYMER

Solids: 50%

SAA level: AEROSOL 102 surfactant- 2.0 phm

Ratio: Vinyl Acetate-85/Butyl Acrylate-13/N-Butoxymethyl Acrylamide-4

I. RECIPE: 952B

A) Kettle charge:

	parts per weight
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DI Water	110
AEROSOL A102 surfactant	6.7
Sodium bicarbonate	1.0
Ammonium persulphate	2.0

B) Monomer charge:

DI Water	75
AEROSOL A102 surfactant	6.7
Sodium methabisulphite	0.4
Vinylacetate	175
Butylacrylate	25
Flush water	15

C) Delayed addition:

NBMA-801-80%	10.4
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II. Glass Transition Temperature:

T_g is calculated as 16.9°C.

III. Procedure:

A) Preparation of kettle charge:

Dissolve 6.7 parts of AEROSOL A102 surfactant, 1.0 parts sodium bicarbonate and 2.0 parts ammonium persulphate in 110 parts of deionized water. Purge the solution with nitrogen while stirring and heat to 65°C.

B) Preparation of monomer charge:

Dissolve 0.4 parts sodium metabisulphite and 6.7 parts AEROSOL A102 surfactant in 75 parts deionized water. Add under sufficient stirring a mix of 175 parts vinylacetate, 25 parts Butylacrylate. Place this monomer pre-emulsion in an addition vessel equipped with stirrer. 10.4 parts NBMA 801 is placed aside.

C) Addition of pre-emulsified monomer to polymerization flask:

When the contents of the polymerization kettle reach 65°C, the nitrogen flow is reduced to a minimum and 15% of the monomer is added to the reactor. After initiation and maximum exotherm, the NBMA solution is added to the monomer emulsion and the addition of monomer emulsion is started at a rate of 1.4 parts per minute. Total addition time requires about 3 - 3½ hours.

Following monomer addition, the addition line is flushed with 15 parts of D.I. water and the latex is held at 65°C for 1 hour, then cooled to room temperature and filtered into a suitable container.

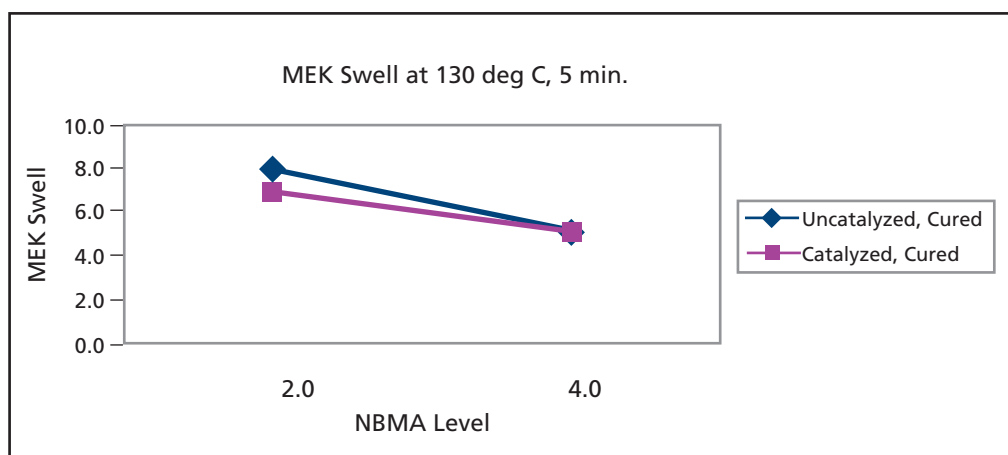
IV. Results:

Parameter	Poly(VA/BA/NBMA-2)	Poly(VA/BA/NBMA-4)
Solids (%)	48.1	48.3
pH	5.0	4.9
PS (nm)	159	155
Viscosity (#1, 20 RPM)	57.0	81.5
Grit 60# (%)	0.01	0.01
Grit 150# (%)	0.001	0.001
Reactor coat (%)	0.02	0.02
Gel Content (%)	1.6	0

V. Film Characteristics:

MEK Swelling @ 130°C,
5 minutes

	Poly(VA/BA/NBMA-2)	Poly(VA/BA/NBMA-4)
Uncatalyzed	7.9	5.12
Catalyzed, pH-3	6.9	5.15



Health and Safety Information

Toxicity

Acute oral (rat) and acute dermal (rabbit) LD₅₀ values are 630 mg/kg and estimated 200-1000 mg/kg, respectively. Mild skin irritation and mild eye irritation were produced during primary irritation studies with rabbits. This material is slightly toxic and the standard precautions normally exercised in handling toxic materials should be followed.

CYLINK NBMA Monomer contains materials which may cause nervous system damage. It also contains formal-dehyde and other materials which caused cancer in laboratory animals. Acrylamide caused male reproductive disorders in laboratory animal tests. Refer to the Cytec Material Safety Data Sheet (MSDS) before using this product.

Handling, Waste Disposal, Spill and Leak Procedures

Utilize a closed system process where feasible.

Where a closed system is not used, good enclosure and local exhaust ventilation should be provided to minimize exposure. After Acrylamide is in solution, exposure to liquid and mist must be controlled. Food, beverages and tobacco products should not be carried, stored or consumed where this chemical is in use. Before eating, drinking or smoking, wash face and hands with soap and water. Shower after completion of workshift. Launder work clothing at end of workshift prior to reuse. Store street clothing separately from work clothing and protective equipment. Work clothing and shoes must not be taken home. Where adequate engineering controls are in effect, and measurements confirm airborne concentrations are below the Permissible Exposure Level, no respiratory protection is required.

NIOSH does not approve a cartridge respirator for use with Acrylamide. However, tests conducted show that organic vapor cartridges provide protection from airborne levels up to 2.5 mg/M3. THE CARTRIDGES MUST BE CHANGED AT THE BEGINNING OF EACH SHIFT. Full facepiece, positive pressure, supplied air respirators or self-contained breathing apparatus must be used for higher or for unknown concentrations. Full facepiece respirators provide additional eye protection where handling makes it desirable. Note that Acrylamide exhibits no warning properties at concentrations at or below the Permissible Exposure Level. Wear the following to prevent skin contact: impervious rubber or plastic gloves, rubber shoes and long sleeved coveralls, which are provided clean daily. For operations where eye and face contact with Acrylamide solution can occur, wear chemical splash-proof goggles, a faceshield and head covering. WASH GLOVES THOROUGHLY BEFORE REMOVING AND DISCARD GLOVES THAT ARE CONTAMINATED ON THE INSIDE. When solutions are used, provide eyewash fountain and safety shower in close proximity to points of potential exposure.

Steps To Be Taken in Case Material is Released or Spilled

1. Remove sources of ignition.
2. Where exposure level is not known, wear NIOSH approved, positive pressure, self-contained respirator. Where exposure level is known, wear NIOSH approved respirator suitable for level of exposure. In addition to the protective clothing/equipment, wear impervious boots. Cover spills with some inert absorbent material; sweep up and place in a waste disposal container. Flush area with water.

TSCA Information

This product is manufactured in compliance with all provisions of the Toxic Substances Control Act, 15 U.S.C.

• Email: custinfo@cytec.com Worldwide Contact Info: www.cytec.com US Toll Free: 800-652-6013 Tel: 973-357-3193 •

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