

Water-borne and air-drying oil-based resins

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Abstract

New water-borne polyurethane resins were produced using maleinized monoglyceride (MMG), hydroxyl-terminated polybutadiene (HTPB), toluene di-isocyanate, and ethylene diamine (EDA). Maleinization was performed in order to insert hydrophilic groups in the fatty acid residues, which were then inserted to the backbone of polyurethane. The MMG was mixed with HTPB in different proportions, and the mixture was used as the polyol part of water-borne polyurethane resin. It was then reacted with toluene di-isocyanate, and the isocyanate end groups were blocked with methyl ethyl ketoxime (MEKO). The ratio of MMG to total polyol was changed between 40 and 70 mol%, while the [NCO]/[OH] ratio was kept at 1.5 in all samples. The carboxylic acid groups of MMG were then neutralized with triethyl amine. The formation of ionic groups imparts water dispersibility. Chain extension was performed by adding EDA and baking at 125 °C. Hardness, adhesion, impact resistance, bending, and abrasion resistance tests were applied to the specimens. The samples exhibited good physical and mechanical properties.

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1. Introduction

Polyurethanes exhibit excellent abrasion resistance, toughness, chemical and corrosion resistance and a wide range of mechanical strengths, thus they have found extensive applications in the high performance coatings for the automotive, appliance, and wood industries [1]. In the 1980s, the automakers started to shift from solvent-based to water-based paints to reduce the amount of volatile combustibles. The increasing trend towards water-dispersed paints accelerated the research on the development of new type of polymeric resins for use in paint industry [2,3]. The research on water-borne paints goes down to early fifties, and the work was mostly concentrated on the use of maleinized oils [4].

Most polyurethane paints available in the market are usually made by using polyester polyols to impart sufficient rigidity to the resin. However, polyether polyols are also used as partial substitute to make resins with improved flexibility. Polyethers increase also the dispersion of the resin in water because they have higher number of hydrophilic groups on

the backbone. The use of polyethylene and polybutylene glycol at appropriate ratios may help to balance the hydrophilic and hydrophobic properties at the desired level. Water-borne alkyds drew continuous attention as the availability of raw materials and the superior properties of the product are concerned. The alkyd resins may also be made water dispersible by mixing a normally synthesized resin with a specially synthesized alkyd which contains high acidic groups. The high acidic groups can be achieved by using a chemical with high functionality such as trimellitic anhydride. The styrenated alkyd may be made water-borne by using hydrophilic monomers such as acrylic acid or methacrylic acid [4]. The research on oil containing water-borne resins is still an active subject in paint industry and new patents were introduced using different raw materials and techniques [5–8]. In recent years, water-dispersed epoxy resins also have gained importance [9]. Although water-dispersed paints display excellent performance in many areas of applications they lack abrasion resistance, chemical resistance and general durability [10]. The research work on water-borne resins and paints cover a wide range from synthesis to characterization [11–15].

Water dispersion of polyurethanes is usually achieved by having carboxyl acid residues on the backbone and quaternizing these groups by tertiary amines. The organic salts thus formed become dispersible in water. The most preferred

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monomer to incorporate hydrophilic group is dimethylol propionic acid though tartaric acid can also be used with some precaution; that is, heavy branching must be prevented during synthesis when tartaric acid is used [14,15]. Polyurethanes contain a soft and a hard segment on the backbone with polyesters (or polyethers) comprising the soft segment, and the urethane group the hard segmental part. Air-drying polyurethane resins can be synthesized by substituting the polyester with monomers containing double bonds on the backbone such as monoglycerides [15]. However, the use of pure monoglyceride results in a thick mixture which is apt to easy gelation. Therefore, it needs to be diluted by using a polyol. The polyol can be of polyester or polyether origin.

The aim of this work was to synthesize water dispersible polyurethane resin containing (i) fatty acid residues to provide air drying and (ii) maleinized fatty acid residues to achieve water dispersion. In other words, the traditionally used dimethylol propionic acid has been substituted by maleinized fatty acids. To improve air drying hydroxyl-terminated polybutadiene (HTPB) was partly used on the backbone. The research work concentrated on synthesizing a maleinized monoglyceride (MMG) derivative from sunflower oil. The monoglyceride derivative contained both fatty acid residues and hydrophilic groups. Two different MMG derivatives were synthesized and the resins made from them were characterized for their properties.

2. Experimental

2.1. Raw materials

The raw materials used were sunflower oil, sodium hydroxide (Merck), sulfuric acid (99.5% pure; Merck), methyl ethyl ketone (99.5% pure; Delta Kimya), toluene sulfonic acid, glycerine (99.5% pure; Birpa Ltd. Ş.), maleic anhydride (Volkan Boya), HTPB (MW = 2700 g/mol; SAGE), toluene diisocyanate (TDI) an isomeric commercial grade mixture (işbir A.Ş.), methyl ethyl ketoxime (MEKO; Volkan Boya), triethylamine (TEA; ÇBS A.Ş.), ethylene diamine (EDA; Merck), and nitrogen gas (99.999% pure; Habaş).

HTPB was dehydrated by passing nitrogen gas through it for 30 h. MEK and MEKO were dehydrated over molecular sieves. MMG, after its production, was dehydrated under vacuum at 50 °C, for about 2 h, and then magnesium sulfate salt was used to remove any remaining water. Other materials were used as-received.

2.2. Synthesis of MMG derivatives

MMG derivative was produced by two different methods. They are denoted here as Method I and Method II. A number of trials were made to synthesize MMG by direct maleinization of monoglyceride. However, gelation took place in all of these trials because of the reaction of anhydride groups

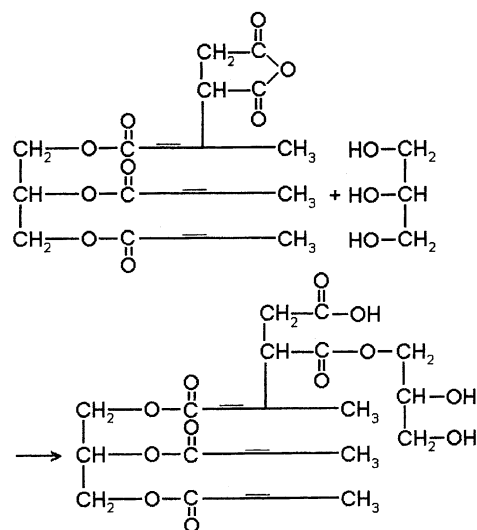
of maleic anhydride and hydroxyl groups of glycerin. In another trial, the oil was maleinized and then reacted with glycerin, but the material gelled in this case too. Therefore, two different methods described below were used to synthesize MMG derivative. The experiments were carried in a 5-necked glass reactor of about 1 l in volume. It is equipped with a stirrer, condenser, thermometer, nitrogen and feed inlet.

2.2.1. Method I

The following steps were performed:

1. The sunflower oil was reacted with maleic anhydride at 200 °C under nitrogen atmosphere for 3 h.
2. The maleinized oil was cooled to 100 °C, and glycerine was added to the reactor. The reaction continued until the acid number came down to a value of 90. As seen in equation the maleinized oil was hydrolyzed with glycerin to yield monoglyceride. It now has two hydroxyl groups to react with a di-isocyanate to make polyurethane, has one carboxylic group that can be used for water dispersion, and two fatty acid residues having double bonds for air drying.

However, this MMG derivative, named MMG-I, resulted in brownish color when used in making polyurethane resin. Therefore, another MMG derivative was synthesized by following another method:



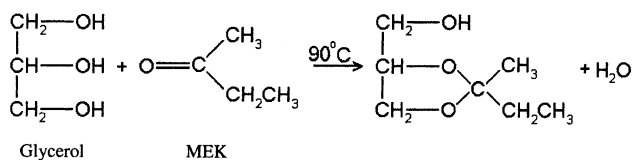
2.2.2. Method II

In this method we needed to use fatty acids in the synthesis of MMG. Therefore, fatty acids were first obtained from the alcoholysis of sunflower oil. The oil was mixed with 1:1 ethanol–water solution, and stoichiometric amount of sodium hydroxide (3 mol per mole of oil) was added. The hydrolysis reaction was carried at 80 °C under reflux until a homogeneous mixture was obtained. The mixture was poured into a saturated solution of sodium chloride in order to precipitate the soap. Then soap was dissolved in water and

reacted with stoichiometric quantity of sulfuric acid. This separates fatty acid phase from water phase. The saturated fatty acids, stearic acid (6 wt.%) and palmitic acid (11 wt.%) with melting points of 69.6 and 63.1 °C, respectively, precipitate at room temperature, and they were filtered out to increase the unsaturation in the final product. The liquid fatty acid phase was washed with water for several times and put under vacuum to remove water.

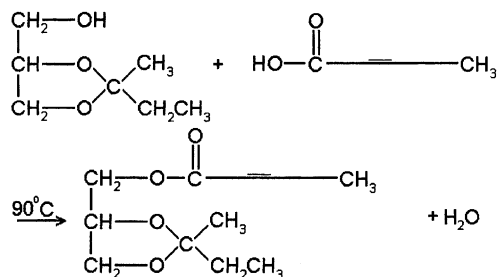
In order to synthesize MMG the following steps were performed:

1. Glycerol was reacted with MEK at 90 °C, using toluene sulfonic acid as a catalyst. Thus two of the hydroxyl groups of glycerine were blocked with MEK:



The reaction water was removed by azeotropic distillation with toluene during reaction.

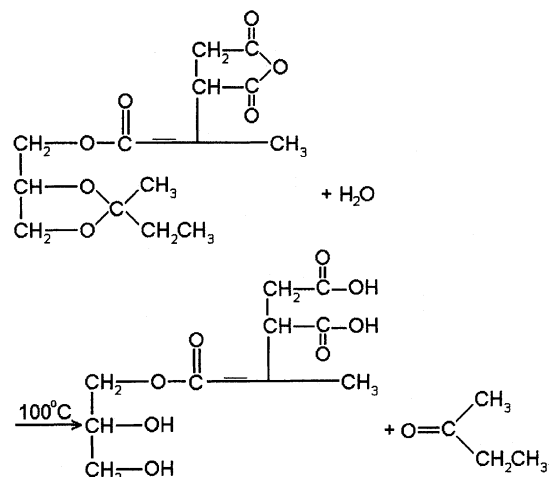
2. The resultant material was reacted with fatty acid mixture using the same catalyst. The fatty acid mixture contains about 35% by weight oleic acid, 62.6% linoleic, and 2.4% linolenic acid. Thus totally unsaturated fatty acid residues are introduced into the structure:



The resulting water was again removed by azeotropic distillation with toluene.

3. The material was washed with water for several times to remove the catalyst. Then, toluene was removed under vacuum.

4. The synthesized chemical was maleinized by reacting it with 30 mol% of maleic anhydride at 200 °C and under nitrogen atmosphere.
5. The maleinized product was hydrolyzed by reacting it with water in the presence of several drops of sulfuric acid, and thus a new maleinized monoglyceride derivative, named MMG-II, was obtained.
6. The MMG derivative was washed with water for several times and then put under vacuum for about 3 h to remove water and MEK produced as a by product:



As the two MMGs are compared, both have two hydroxyl groups, MMG-I has one carboxyl group while MMG-II has two. MMG-I has an additional two more fatty acid residues. The molecular weight of MMG-I is 1053 g/mol, and that of MMG-II is 455 g/mol.

2.3. Water-dispersed polyurethane varnish production

In all experiments, the [NCO]/[OH] ratio was kept at 1.5 in order to assure NCO termination of the prepolymer. The experiments were repeated by changing the ratio of MMG to HTPB. Several formulations of the feed are given in Table 1. The following procedure was carried out in making water-dispersed polyurethane:

1. HTPB and MMG were dissolved in MEK by stirring the mixture for 30 min at 50 °C. This was done in

Table 1
Basic formulations of the resin

Method	Sample	Ratio ^a (%)	MMG (mol)	HTPB (mol)	TDI (mol)	MEKO (mol)	TEA (mol)	EDA (mol)
I	A1	40	0.8	1.2	3.0	2.0	0.8	1.0
I	A2	50	1.0	1.0	3.0	2.0	1.0	1.0
I	A3	60	1.2	0.8	3.0	2.0	1.2	1.0
I	A4	70	1.4	0.6	3.0	2.0	1.4	1.0
II	B1	50	1.0	1.0	3.0	2.0	0.6	1.0
II	B2	55	1.1	0.9	3.0	2.0	0.66	1.0
II	B3	60	1.2	0.8	3.0	2.0	0.72	1.0
II	B4	65	1.3	0.7	3.0	2.0	0.78	1.0
II	B5	70	1.4	0.6	3.0	2.0	0.84	1.0

^a MMG/(MMG + HTPB).

order to have a homogeneous distribution of hydrophilic molecules in the polymer backbone.

2. TDI was added to the mixture and the reaction continued for 3 h with stirring at 70 °C. The reaction time was determined by using di-butylamine back titration method.
3. After the completion of the reaction, the prepolymer was cooled to 50 °C, and the free NCO groups of the prepolymer were blocked with MEKO for approximately 2 h. This step is not necessary. However, it is done to improve the shelf-life of the resin.
4. TEA was added to the solution to neutralize the carboxylic groups, and the mixture was stirred for 30 min, while maintaining the temperature at 50 °C.
5. Water was added to the solution at an amount to make 50% of the total mass from a stop-cock burette by one drop per two or three seconds under continuous stirring.

3. Results and discussion

3.1. Chain extension by baking

Ethylene diamine was used for the chain extension of blocked isocyanate groups. It was added at stoichiometric amounts to all samples prepared. It was added 2–3 h before the application step because it causes gelation at room temperature in 4 days after its addition.

3.2. Preparation of test panels

A standard of 30 μm wet film thickness was applied to test panels. This was done by using film casting knife (Braive-Instruments) on the panels. After casting, the test panels were put in an oven, where the temperature was increased to 125 °C, and maintained at this temperature for 3 h. The varnishes which were produced using MMG produced through Method II required a temperature of 175 °C to form a non-tacky film. The films dried in 1 day at room temperature without using any drier.

3.3. NMR spectroscopy

A Bruker-Spectrospin Avance (DPX 400) Ultra-Shield Nuclear Magnetic Resonance instrument was used to characterize the MMG. The characterization by using ^1H NMR spectroscopy was done only for MMG-II because the process used is a novel one. The characterization was done by comparing the spectroscopy of a mixture of maleic anhydride and monoglyceride in Fig. 1 with that of MMG in Fig. 2.

The results showed that the double bonds of MMG disappeared after the reaction. In Fig. 1, the peak at 6.2 ppm denotes the double bonds of maleic anhydride, and it disappeared after the reaction of maleic anhydride with monoglyceride as shown in Fig. 2. The other peaks appear in both figures because they have similar structure. The peak

at 5.2 ppm denotes the hydrogen atom bonded to the secondary carbon atom in the monoglyceride molecule. This peak covers also carbon–carbon double bond of the fatty acid residue. The peak at 4.1 ppm denotes the carboxylic and ester groups. The peak at 2.6 ppm corresponds to $-\text{CH}_2-$ groups adjacent to double bond in the fatty acid residue, and the one at 2.25 ppm denotes the $-\text{CH}_2-$ groups adjacent to the ester bond and the groups that are not bonded to the carbon atoms in the double bonds. The peak at 2.0 ppm corresponds to the $-\text{CH}_2-$ from maleic anhydride, and the one at 1.3 ppm denotes the $-\text{CH}_2-$ groups adjacent to methyl groups in the fatty acids and methyl ethyl ketone. The peak at 0.9 ppm denotes the $-\text{CH}_3$ group in the fatty acid and methyl ethyl ketone.

3.4. IR spectra

Hitachi (Model: 270-30) Infrared Spectrophotometer was used to characterize the samples. The IR spectrum of MMG-I and of MMG-II are shown in Figs. 3 and 4, respectively.

The peak at 3500 cm^{-1} corresponds to OH stretching, the small shoulder at 3000 cm^{-1} corresponds to unsaturated CH stretching, and the peak at 2900 cm^{-1} corresponds to CH_2 stretching. The peak at 1720 cm^{-1} corresponds to C=O stretching of ester, and the shoulder at 1700 cm^{-1} to C=O stretching of carboxylic group from maleic anhydride. The peak at 1460 cm^{-1} is due to $-\text{CH}_3$ bending and the broadening in the peak is due to *cis* C=C group. The peak due to $-\text{CH}_3$ bending exists at 1380 cm^{-1} , the peak at 1170 cm^{-1} corresponds to C–O–C stretching of ester, and the peak at 720 cm^{-1} is due to multiple CH_2 split from $(\text{CH}_2)_n$.

Both figures look similar, however, it can be noticed that in Fig. 3 the peaks at 3000 cm^{-1} has higher intensity and it is merged into the adjacent peak. This difference is due to the higher concentration of fatty acid residues with unsaturated bonds. The higher intensity of the peak below 1800 cm^{-1} shows the higher concentration of carboxylic groups from maleic anhydride. The higher intensity at 920 cm^{-1} is due to the higher dimer content because of the higher carboxylic acid groups.

Figs. 5 and 6 show the IR spectrum of the polyurethane produced by using MMG-I and MMG-II, respectively. The urethane bond was characterized by the presence of NH group at $3300\text{--}3500\text{ cm}^{-1}$. The peak at 2900 cm^{-1} is due to the CH stretching, and the peak at 1720 cm^{-1} corresponds to C=O stretching from ester groups. The other peaks are from the raw materials used. The absence of peaks in the range $2000\text{--}2300\text{ cm}^{-1}$ shows that all isocyanate groups were involved in the reaction, and that there are no significant isocyanate groups in the resin.

3.5. Color of the dry films

The varnish produced by using MMG-II, gave slightly yellow transparent films. On the other hand, the varnish produced from MMG-I gave brown and semitransparent films.

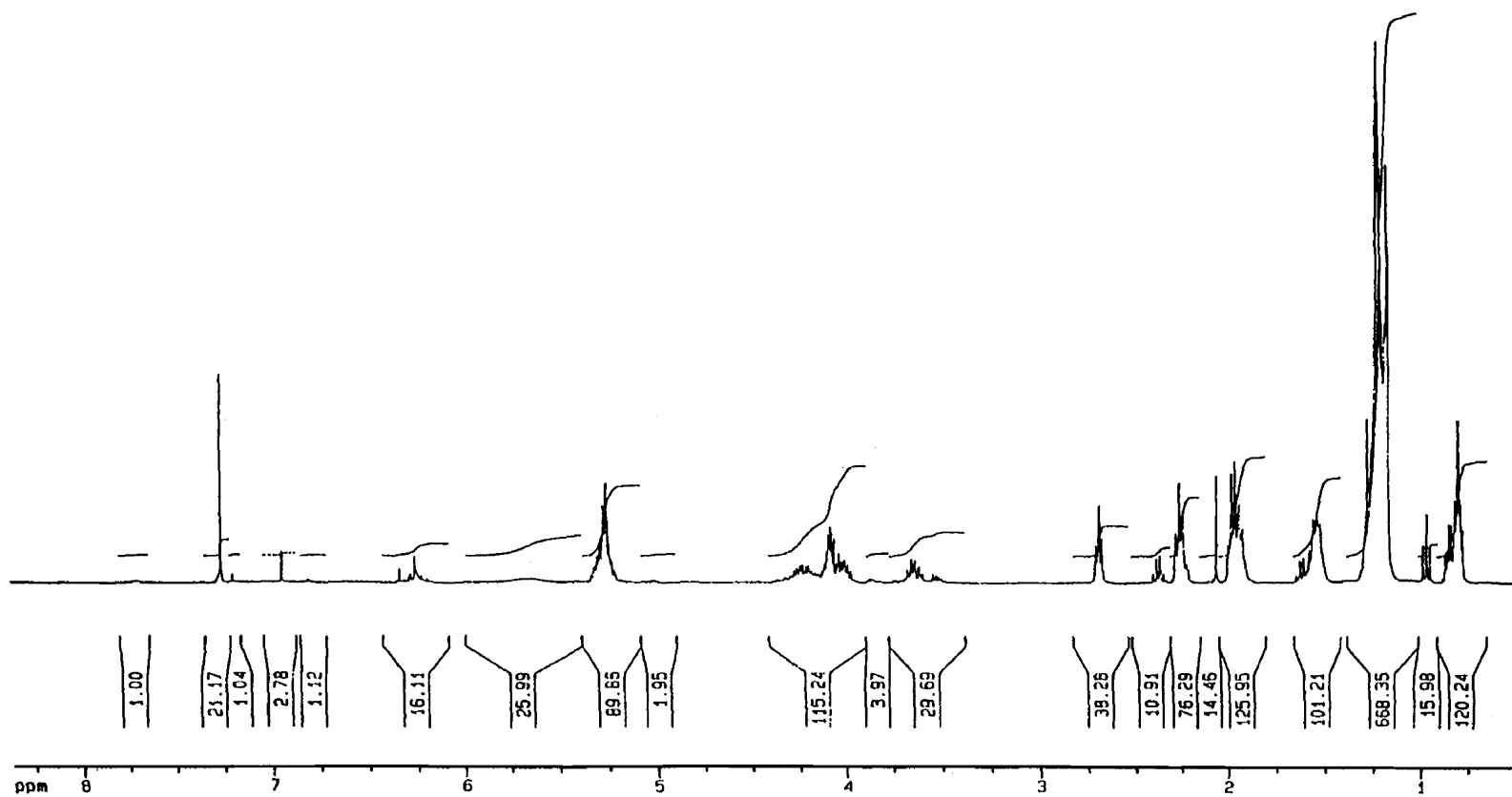


Fig. 1. NMR of monoglyceride and maleic anhydride mixture.

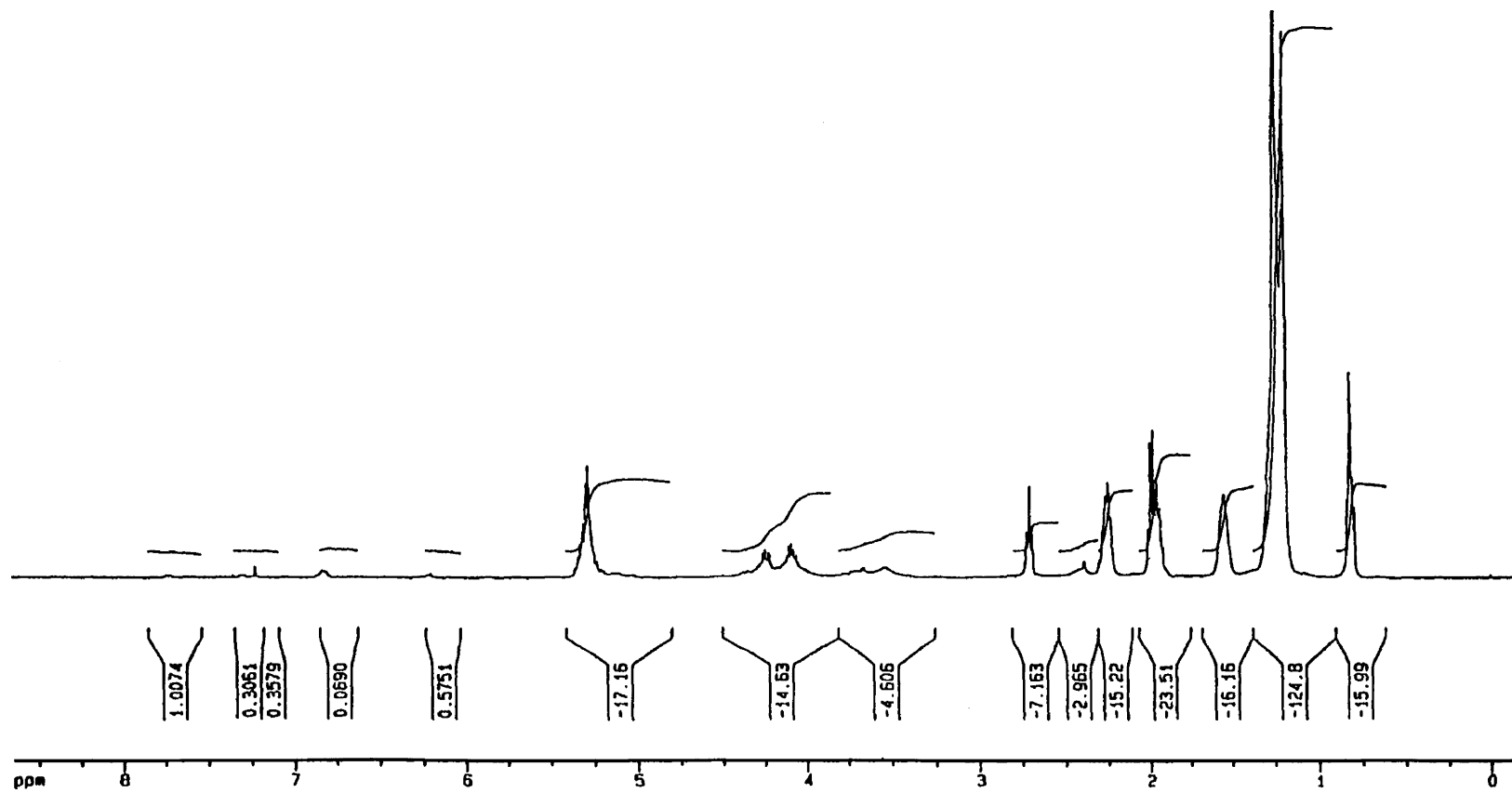


Fig. 2. NMR of MMG.

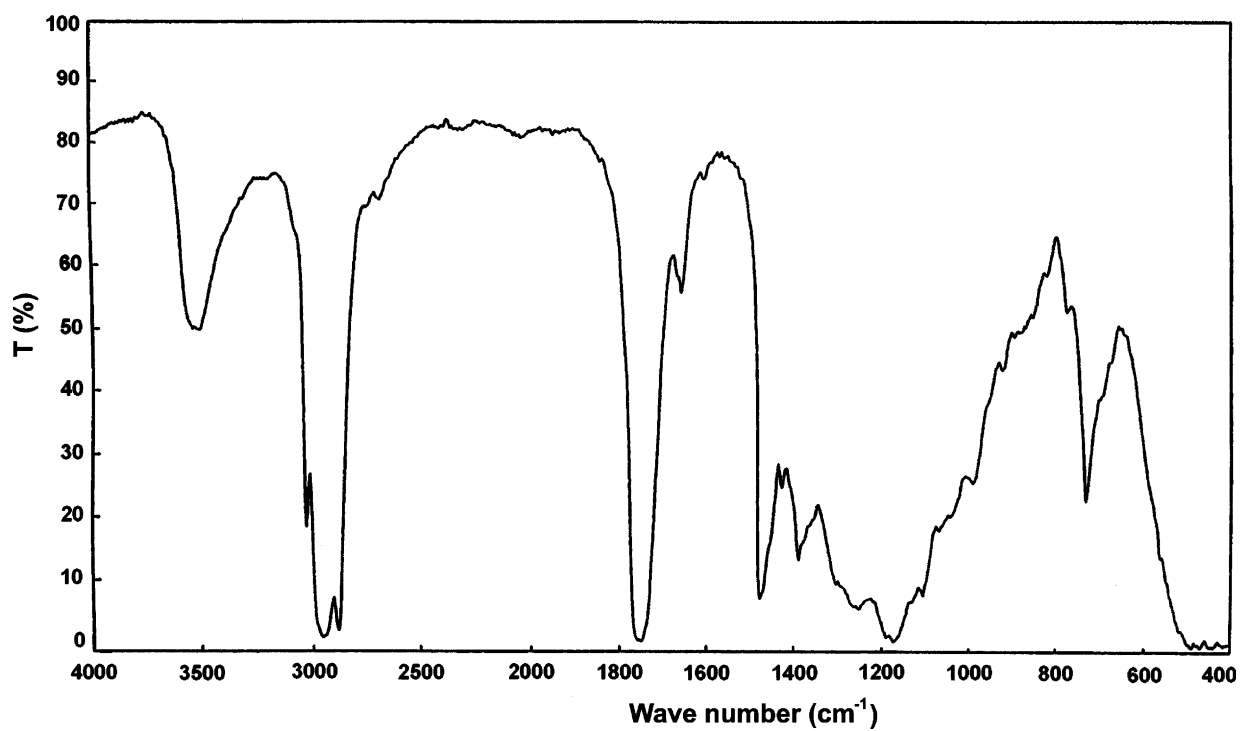


Fig. 3. IR of MMG produced by Method I.

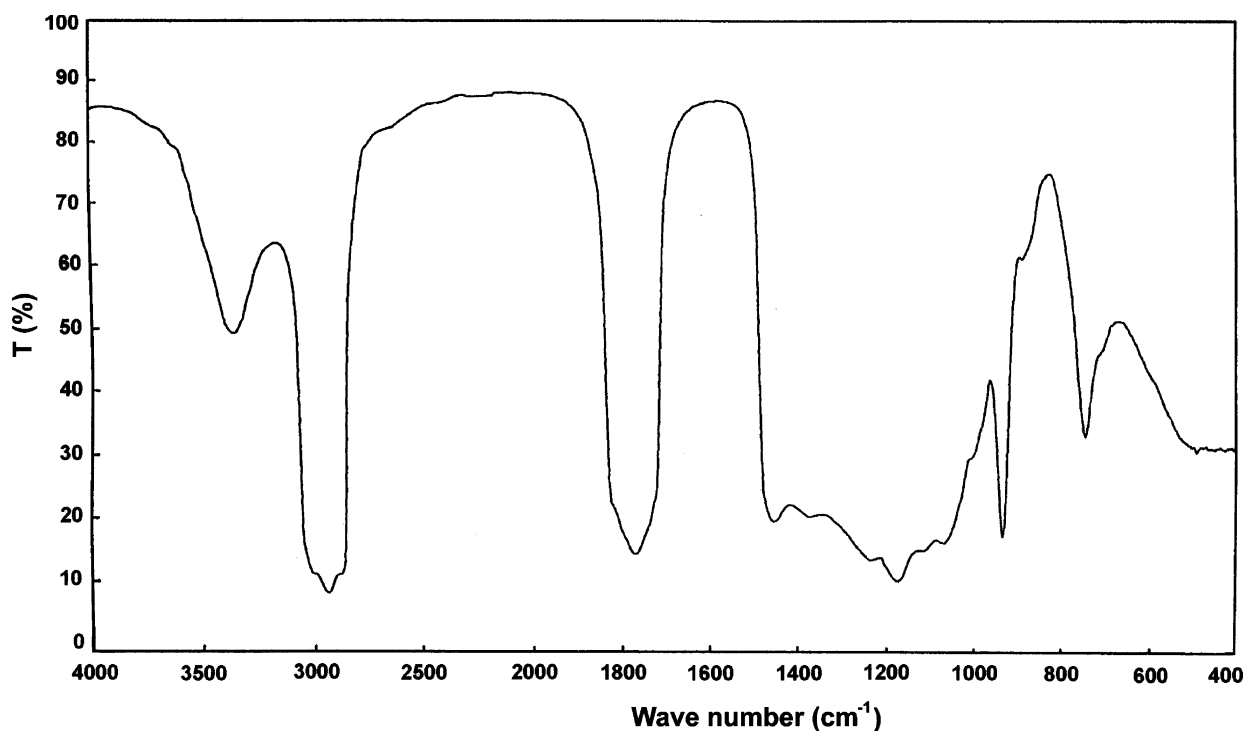


Fig. 4. IR of MMG produced by Method II.

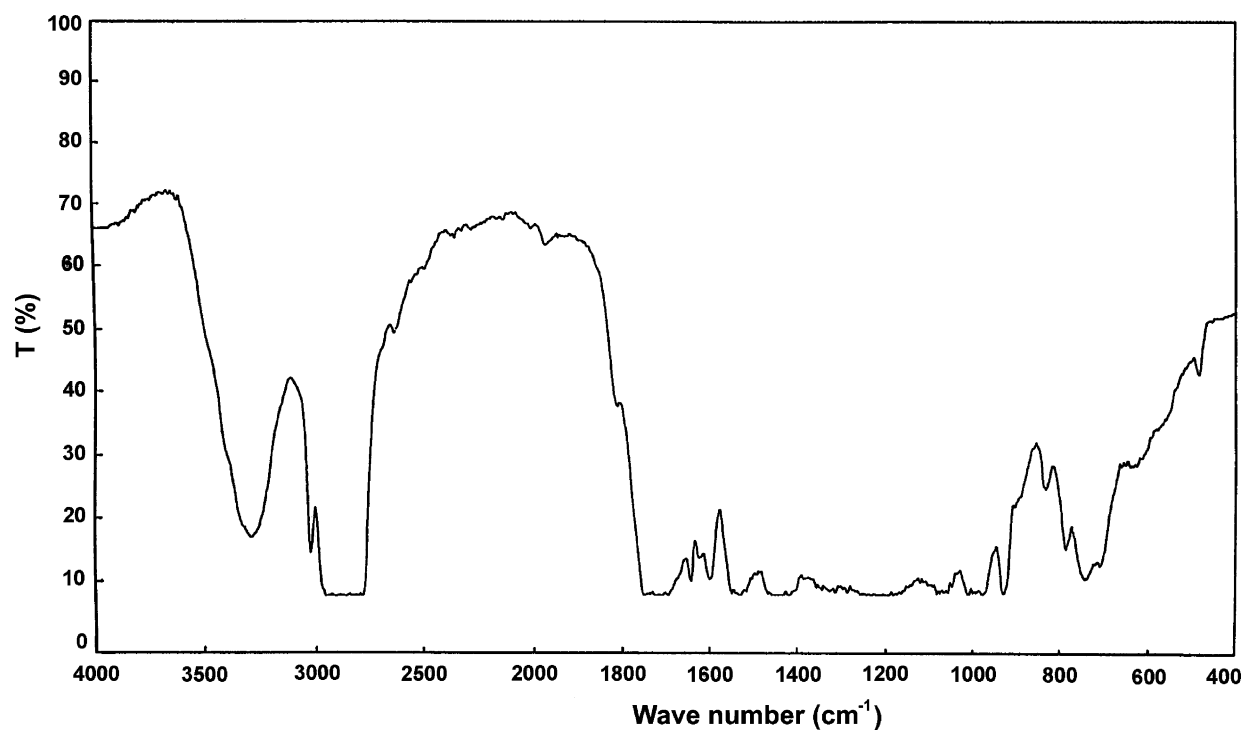


Fig. 5. IR spectrum of dry film of Sample A2.

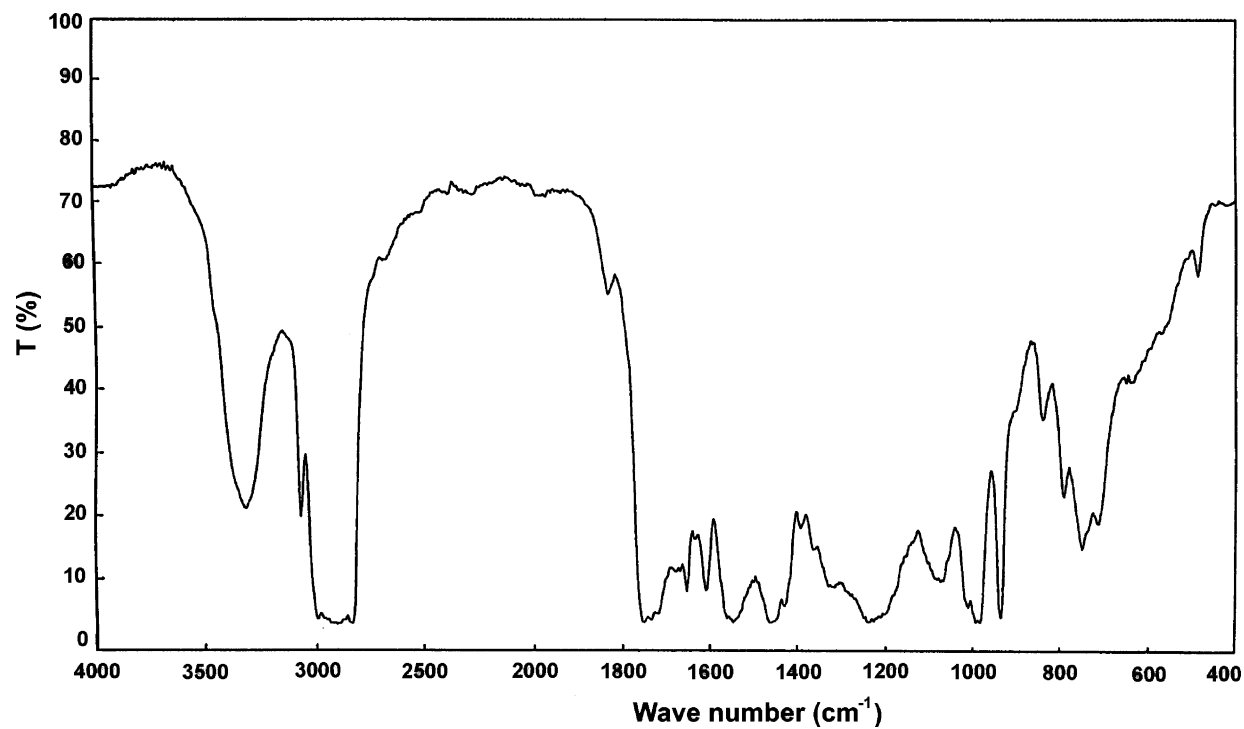


Fig. 6. IR spectrum of dry film of Sample B1.

Table 2
Gloss values for the samples

Method	Sample	Gloss value (%)		
		20°	60°	85°
I	A1	64.5	75.6	35.3
I	A2	21.0	53.2	48.0
I	A3	57.8	87.0	73.5
I	A4	25.5	55.0	49.2
II	B1	97.1	96.7	96.0
II	B2	86.8	90.3	95.0
II	B3	98.8	93.0	92.1
II	B4	78.3	89.0	87.3
II	B5	91.7	98.0	98.2

This difference is apparently due to higher ratio of fatty acid residues in the MMG produced by Method I.

3.6. Gloss test

A Rhopoint-Novoglass glossmeter was used to test the light reflection properties of the specimens. The gloss of dry films was measured at 20°, 60°, and 85°. The results were listed in Table 2. These results show that varnishes produced by using MMG-II had excellent gloss.

3.7. Hardness test

A Braive-Instrument Persoz Pendulum (No. 3034) was used. The principle of this test is based on the fact that the increase of hardness decreases the effect of friction, which increases the number of oscillations of the pendulum swinging on the test panel.

The dependence of hardness on the amount of MMG in the polymer can be seen in Figs. 7 and 8 for the varnishes produced by using MMG-I and MMG-II, respectively. In Fig. 7, the hardness decreases as the amount of MMG increases at all ratios used, while in Fig. 8 it first increases then decreases after 55% of MMG content. The decrease

of the amount of MMG results in a relative increase in the amount of HTPB. The double bond content of monoglyceride is about 1 per 9 carbon atoms and that of HTPB is about 1 per 4 carbon atoms. Therefore, HTPB gives denser cross-linking which results in higher hardness. It is also noticed that the varnish produced by using MMG-II has about twice higher hardness than that produced by using MMG-I. This is because MMG-I contains three fatty acid residues per molecule that makes the resin softer on drying whereas MMG-II contains only one fatty acid residue per molecule.

The decrease of hardness below 55% MMG in Fig. 8 can be due to the fact that hardness decreases with the increased branching. Branching in the polymer is due to the pendant fatty acid residues which come from MMG. The increase in the quantity of fatty acids increases side branches. There are two different cross-linkings which influence hardness: (i) the cross-linking due to double bonds of HTPB on the backbone and (ii) the cross-linking due to double bonds of fatty acid residues which are short branchings. As MMG decreases HTPB increases, so the double bonds on the backbone increase and the double bonds on the side branches decreases, or vice versa. The optimum ratio that balances both sources of hardness is 55% MMG in MMG-II containing varnish.

3.8. Mandrel bending test

A conical mandrel bending tester (Braive-Instruments No. 1510) was used. After coating the panels with the paint at a uniform thickness, they were fastened and bent over, and cracks were observed along the increasing radius of the conical mandrel. All samples passed bending test successfully without any cracks in the bent film. This is mainly due to the flexibility of the film which is a characteristic feature of polyurethanes.

3.9. Impact resistance test

A Gardner Impact tester (Model: 5510) was used for this test. A standard weight of (1+0.9 kg) was dropped on a film

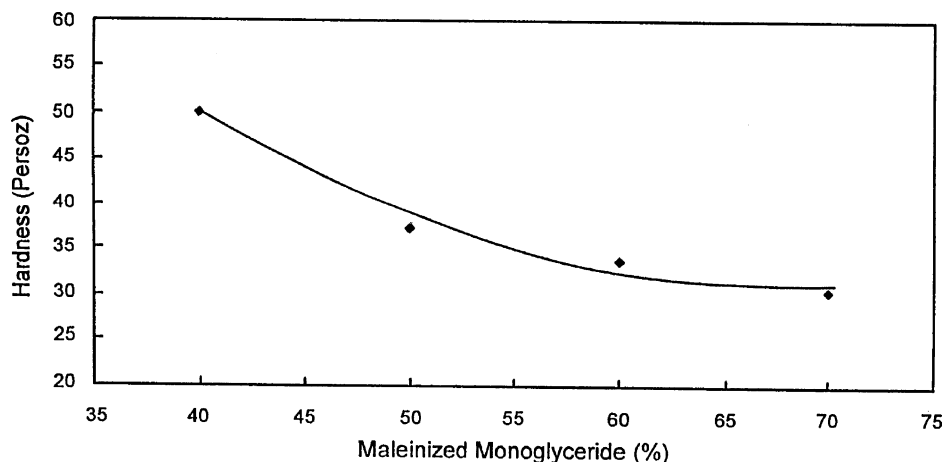


Fig. 7. Change of hardness with the percent of MMG-I in "MMG + HTPB".

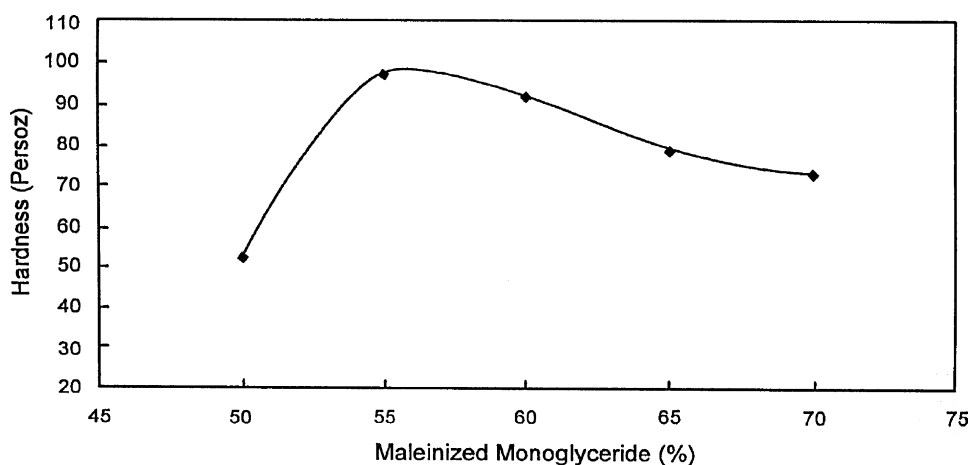


Fig. 8. Change of hardness with the percent of MMG-II in "MMG + HTPB".

coated on a metal plate from different heights. The impact value at which the film cracks is considered as the impact value for that sample. All tested samples showed resistance to impact up to 20 J which is the upper limit used without cracking.

3.10. Adhesion test

A crosshatch cutter was used to cut the film to produce a lattice pattern. After making a cross cut, the coating film was brushed with a soft tissue to remove any detached flakes of coating. Then, the pattern was checked according to ASTM D 3359 B. The maximum number of adhesion is "5" and the minimum is "0". Adhesion was tested on both a metal and a glass surface.

The adhesion test values for the samples are shown in Table 3. These results show that varnishes produced through Method I gives better adhesion than those produced through Method II. This is because MMG produced by Method I contains higher ratio of fatty acid residues, which improves adhesion. Also, it is obvious that Samples B1–B5 have better adhesion on metal plates than on glass plates.

Table 3
Adhesion test

Method	Sample	Adhesion number	
		Metal plate	Glass plate
I	A1	5 B	5 B
I	A2	5 B	5 B
I	A3	5 B	5 B
I	A4	5 B	5 B
II	B1	4 B	3 B
II	B2	5 B	0 B
II	B3	1 B	2 B
II	B4	1 B	1 B
II	B5	4 B	1 B

3.11. Abrasion resistance test

This test determines the resistance of coating film toward a falling abrasive. The abrasive is allowed to fall from a specified height through a guide tube onto a coated panel until the substrate becomes visible. The amount of abrasive per unit film thickness is reported as the abrasion resistance of the coating film. Silica sand was used as abrasive. All samples tested showed very good abrasion resistance and no significant loss in film thickness was observed.

4. Conclusions

1. The MMG-I containing varnish had darker color and lower gloss than the one that contains MMG-II.
2. In general, hardness showed a decreasing trend as the MMG ratio in the polyol increased.
3. The MMG-II-based varnish had higher hardness values than MMG-I-based varnish.
4. The optimum hardness in MMG-II-based varnish was achieved at 55% MMG ratio. This ratio may correspond to the optimum balance between the double bonds of HTPB and fatty acid residues.
5. The samples in which MMG-I was used showed much better adhesion compared to those in which MMG-II was used.
6. All samples tested for impact resistance showed resistance above 20 J.
7. All the tested samples passed conical mandrel bending test without any cracks.
8. No detectable loss in film thickness was observed after the abrasion resistance test.

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