

Synthesis of Water-Reducible Acrylic–Alkyd Resins Based on Modified Palm Oil

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Received 23 December 2003; accepted 31 May 2004

DOI 10.1002/app.21009

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Water-reducible acrylic–alkyd resins were synthesized from the reaction between monoglycerides prepared from modified palm oil and carboxy-functional acrylic copolymer followed by neutralization of carboxyl groups with diethanolamine. Modified palm oil was produced by interesterification of palm oil with tung oil at a weight ratio of 1 : 1, using sodium hydroxide as a catalyst, whereas carboxy-functional acrylic copolymer was prepared by radical copolymerization of *n*-butyl methacrylate and maleic anhydride. The amount of acrylic copolymer used was from 15 to 40% by weight, and it was found that homogeneous resins

was obtained when the copolymer content was 20–35 wt %. All of the prepared water-reducible acrylic–alkyd resins were yellowish viscous liquids. Their films were dried by baking at 190°C and their properties were determined. These films showed excellent water and acid resistance and good alkali resistance. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1170–1175, 2005

Key words: palm oil; interesterification; water reducible coatings; alkyd resins; carboxy-functional acrylic copolymer

INTRODUCTION

Alkyds, synthetic resins widely used in surface coating industries, are polyesters synthesized from the reaction between polyhydric alcohols, such as glycerol, and di- or poly-basic acids (or their anhydrides), such as phthalic anhydride. Fatty acids or vegetable oils are usually added to the resins to improve the flexibility and their solubility in hydrocarbon solvents.^{1,2} Furthermore, alkyd resins can be made water-reducible by introducing carboxyl groups along the polymer backbone and using salts of their carboxyl groups to stabilize them as aqueous dispersions.^{3,4}

Palm oil, the highest domestically produced vegetable oil in Thailand, was used in this research. However, because of its lack of di- and triunsaturated fatty acid components, which are responsible for the curing reaction, it was necessary to modify the composition of palm oil. Interesterification is one of the important processes that is used to modify the structure and composition of vegetable oils.^{5–9} In this process, the distribution of fatty acids is rearranged on the glycerol backbone as shown in Scheme 1 (where R = fatty acid chain).

Thus, in this work, palm oil was initially modified by an interesterification with tung oil and the resulting

modified palm oil was used for the production of alkyd resin.

Alkyd resins have many advantages over other resins, such as good heat and solvent resistances, excellent gloss, and low cost. However, the disadvantages of these resins are their low water, acid, and alkali resistances. These disadvantages can be improved by adding resins having excellent water, acid, and alkali resistances, such as acrylic resin.^{10,11} Therefore, in this research, carboxy-functional acrylic copolymer was used instead of di- or poly-basic acids for synthesis of acrylic–alkyd resins having some unreacted carboxyl groups. Further, the carboxyl groups can be neutralized by a base to give water-reducible resins. A reaction scheme for the preparation of water-reducible acrylic–alkyd resins is shown in Figure 1.

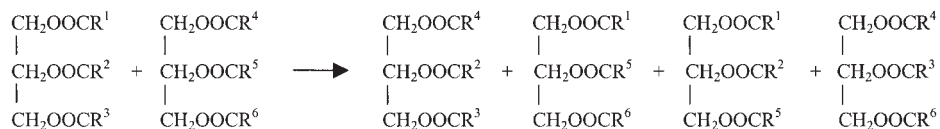
EXPERIMENTAL

Materials

Maleic anhydride (MA), *n*-butyl methacrylate (BMA), benzoyl peroxide (BPO), methanol, sodium hydroxide (NaOH), glycerol, ethanol, and diethanolamine were purchased from Fluka Chemika (Buchs, Switzerland). Refined tung oil and refined palm oil were donated from Note Printing Works, Bank of Thailand and Morakot Industries Co., Ltd. (Samutprakarn, Thailand), respectively. Xylene was purchased from Labscan Asia (Bangkok, Thailand). All materials were used as received without further purification.

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Contract grant sponsor: Chulalongkorn University, Thailand.



Scheme 1

Methods

Synthesis and characterization of acrylic copolymer

MA (35 g) and xylene (100 mL) were mixed in a 500-mL four-neck round-bottom flask, equipped with

a stirrer, a thermometer, a condenser, and N₂ gas inlet. The mixture was stirred at 95°C under nitrogen atmosphere and a solution of BPO (2 g) in BMA (65 g) was continuously added to the mixture within 2 h. After that, the mixture was stirred at this temperature for

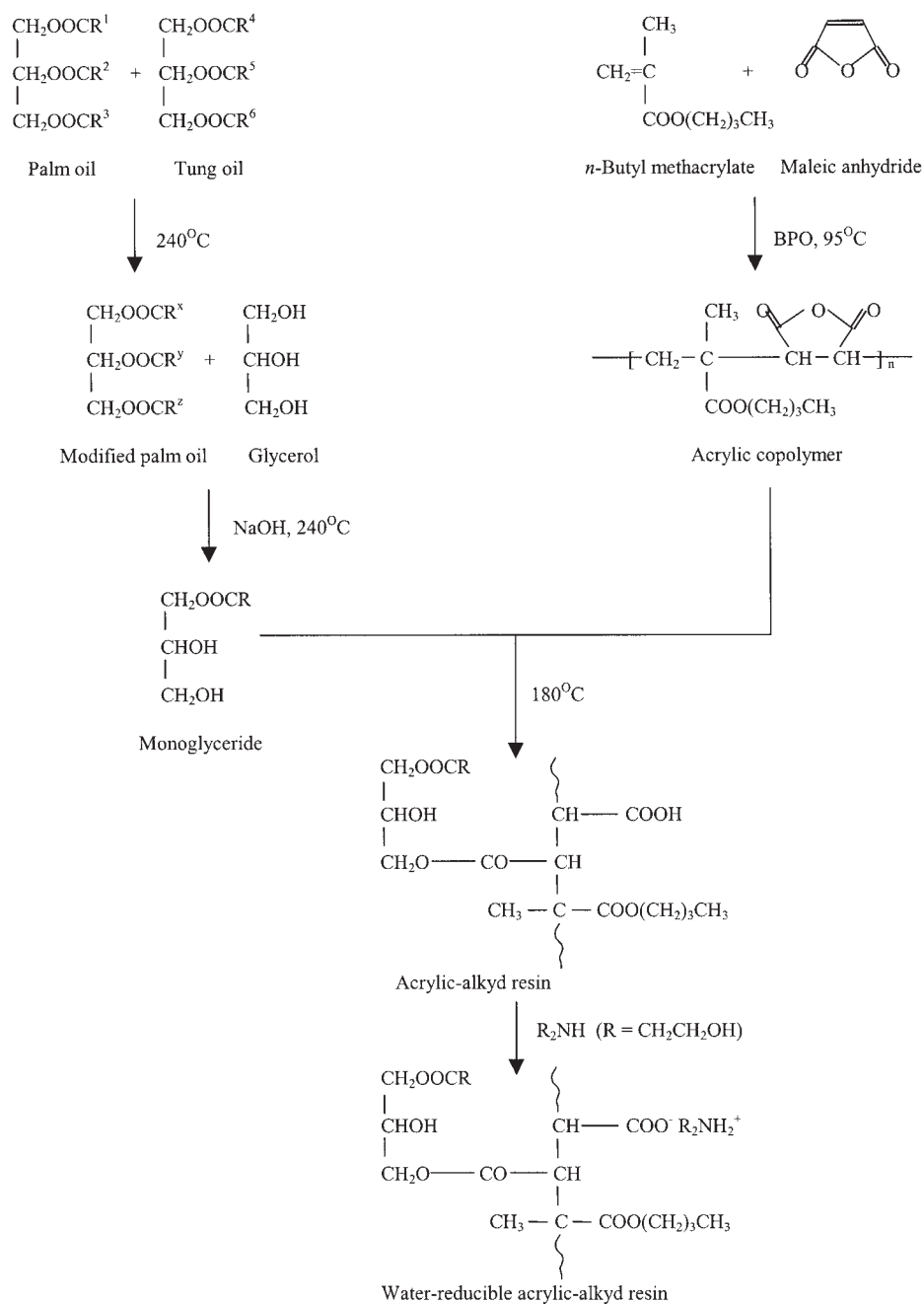


Figure 1 Scheme for synthesis of water-reducible acrylic-alkyd resin.

TABLE I
Amounts of Monoglyceride and Acrylic Copolymer Used
in the Synthesis of Acrylic-Alkyd Resins

Weight of monoglyceride (g)	85	80	75	70	65	60
Weight of acrylic copolymer (g)	15	20	25	30	35	40

another 2 h. It was then cooled to room temperature under nitrogen atmosphere and poured into methanol to precipitate the product. The chemical structure of the obtained product was analyzed using a Nicolet FTIR spectrophotometer (Model Impact 400; Nicolet Analytical Instruments, Madison, WI). Its molecular weight and molecular weight distribution were also characterized by GPC (Model Waters 150-CV, Waters Corp., Milford, MA) using THF as solvent with an injection rate of 1 mL/min at 30°C. Its acid value was calculated based on ASTM D1639.

Synthesis and characterization of modified palm oil-based monoglycerides

Palm oil (50 g) and tung oil (50 g) were mixed in a 500-mL four-neck round-bottom flask, equipped with a stirrer, a thermometer, a condenser, a water separator, and N₂ gas inlet. NaOH (0.1% w/w) was added and the mixture was stirred at 240°C under nitrogen atmosphere for 90 min. After that, glycerol (25.5 g) and NaOH (0.1 g) were added and the mixture was stirred at 240°C under nitrogen atmosphere and maintained at this temperature until a sample (one part) was soluble in ethanol (three parts), indicating the formation of the monoglyceride. The obtained product was allowed to cool to room temperature under nitrogen atmosphere and its chemical structure was analyzed using a Nicolet FTIR spectrophotometer (Model Impact 400).

Synthesis and characterization of water-reducible acrylic-alkyd resins

Monoglyceride and acrylic copolymer at desired amounts, as given in Table I, were mixed in a 500-mL four-neck round-bottom flask, equipped with a stirrer, a thermometer, a condenser, a water separator, and N₂ gas inlet. The mixture was stirred and heated to 180°C within 20 min and was then immediately cooled to room temperature under nitrogen atmosphere to obtain an acrylic-alkyd resin.

The acrylic-alkyd resin was neutralized by diethanolamine at 70°C. After that, deionized water (60 wt % of the final total weight) was continuously added to the neutral resin within 1 h at 70°C. The mixture became a high viscosity white opaque liquid at first. As more water was added, the viscosity of the mixture decreased. After completion of water addition, the mixture was stirred at this temperature for another 1 h. The mixture was then allowed to cool to room temperature and the water-reducible resin was obtained.

The viscosities of the acrylic-alkyd resins were determined using a Brookfield viscometer (Model RVT; Brookfield Engineering Laboratories Inc., Stoughton, MA).

The chemical structures of the resins and their corresponding water-reducible products were determined using a Nicolet FTIR spectrophotometer (Model Impact 400). Their acid values were calculated based on ASTM D1639.

The colors of the water-reducible resins were determined by comparison with the colors of standard Gardner solutions. Their drying times (with wet film thickness of 30 μm) were determined based on ASTM D1640.

Percentage nonvolatile content (%NV) of the resins was calculated from the following equation after drying the sample at 105°C for 3 h:

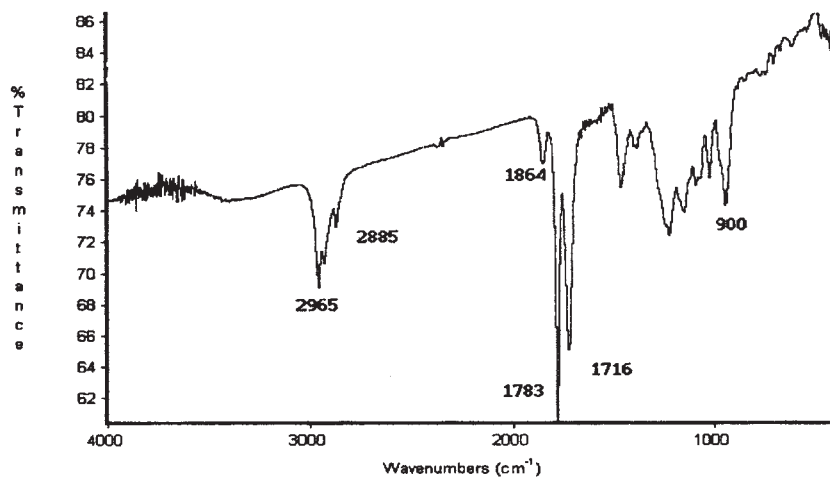


Figure 2 FTIR spectrum of synthesized acrylic copolymer.

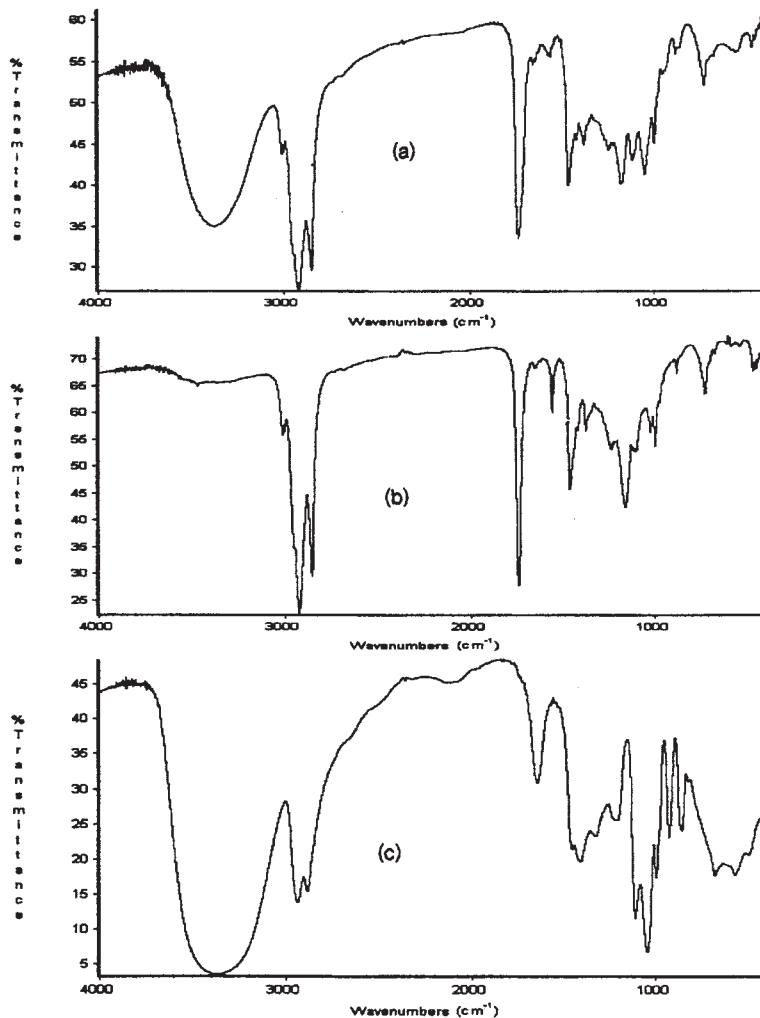


Figure 3 FTIR spectra of monoglycerides (a), modified palm oil (b), and glycerol (c).

$$NV = 100 - [(A - B)/A \times 100]$$

Determination of film properties

where *A* is the weight of the sample before drying and *B* is the weight of sample after drying.

The films were formed by applying the resins on tin plate or glass panels depending on each standard test

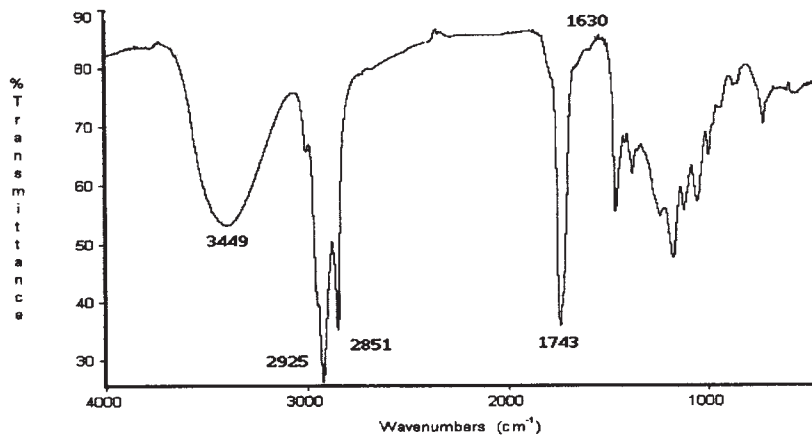


Figure 4 FTIR spectrum of synthesized acrylic-alkyd resin.

TABLE II
Viscosities and Acid Values of Synthesized
Acrylic-Alkyd Resins

Acrylic content in resin (wt %)	Viscosity (poise)	Acid value
20	8,000	17.4
25	8,500	22.4
30	9,000	24.7
35	10,000	28.4

TABLE III
Characteristics of Synthesized Water-Reducible Acrylic-
Alkyd Resins

Type of alkyd resins	Color (Gardner)	%NV	Acid value
20% acrylic	10.5	34.75	0.3
25% acrylic	10.5	34.01	0.5
30% acrylic	10.5	33.15	0.7
35% acrylic	10.5	33.52	1.0

method using a film applicator. The samples were then subjected to the following tests including flexibility using a conical mandrel test apparatus (Sheen Instruments Ltd., Surrey, UK), adhesion using a cross-cut tape method based on ASTM D3359 Method B, and impact resistance using an impact tester (Sheen Instruments). Furthermore, water, acid, and alkali resistances were also analyzed based on ASTM D1647.

RESULTS AND DISCUSSION

BPO-initiated free-radical copolymerization of BMA and MA yielded 87.18% of white powder of acrylic copolymer having number-average molecular weight and molecular weight distribution of 6960 and 1.97, respectively. The FTIR spectrum of acrylic copolymer was recorded to confirm the structure of copolymer, as shown in Figure 2. A strong band at 1716 cm^{-1} can be attributed to the ester groups of BMA, whereas the presence of carbonyl groups of MA is confirmed by a very strong band at 1783 cm^{-1} (symmetric stretching) and a weak band at 1864 cm^{-1} (asymmetric stretching). This acrylic copolymer had an acid value of 113.7.

The FTIR spectrum of monoglycerides obtained from alcoholysis of modified palm oil with glycerol is shown in Figure 3(a). It is clearly seen that it exhibits

both characteristic peaks of hydroxyl groups and methylene groups compared to the FTIR spectra of modified palm oil [Fig. (3b)] and glycerol [Fig. (3c)].

Acrylic-alkyd resins, synthesized from the reaction between acrylic copolymer and monoglycerides using acrylic copolymer at 20–35 wt %, were yellowish viscous liquids. Gelation occurred when the acrylic copolymer content was 40 wt %, which can be explained as follows: when a mixture of 60% w/w monoglyceride with 40% acrylic copolymer has a hydroxyl/carboxyl ratio of about 1, the molecular weight would increase rapidly at high conversion, thus causing excessive viscosity buildup and, finally, leading to gelation. On the other hand, when the acrylic copolymer content was 15 wt %, the sol-gel mixture was observed, which can be explained as follows: a mixture of 85% w/w monoglyceride and 15% of the acrylic copolymer led to an overwhelming excess of hydroxyl groups, leading to an inhomogeneous mixture of products.

An example of FTIR spectrum of these acrylic-alkyd resins is shown in Figure 4. It can be seen that the resin exhibits the carbonyl characteristic peak of ester linkages at 1743 cm^{-1} . The viscosities and acid values of these resins are given in Table II. The results show that as acrylic content in the resin increases, the viscosity of

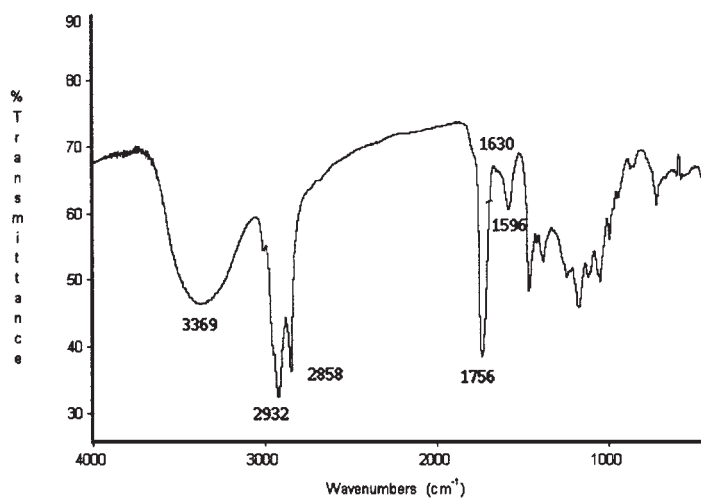


Figure 5 FTIR spectrum of synthesized water-reducible acrylic-alkyd resin.

the resin increases, indicating an increase in molecular weight of the resin.

After neutralization of acrylic-alkyd resins with diethanolamine and dissolving neutral product in deionized water, the obtained water-reducible acrylic-alkyd resins were yellowish transparent liquids having characteristics as given in Table III. It can be seen that acid values of all the prepared acrylic-alkyd resins are very low because of the higher amounts of hydroxyl groups than that of carboxyl groups. Consequently, the water-reducible property is attributed to not only the salts of carboxyl groups but also the presence of the hydroxyl groups.

A sample FTIR spectrum of these resins, in Figure 5, shows peaks corresponding to carboxylate anion stretching at 1596 cm^{-1} . It was observed that the intensity of these peaks increases as the amount of acrylic copolymer in the resins increases.

After applying water-reducible acrylic-alkyd resins on the substrates to determine their drying times, it was found that the films were not cured very well after air drying for 10 days. This phenomenon can be related to the presence of water and diethanolamine, which normally inhibit the oxidation and some crosslinking reaction. Furthermore, previous studies showed that increased active drier levels are required for water-reducible alkyds because both the neutralizing base and the presence of water contribute to slower drying time.¹² Therefore, by adding 2 wt % of Co-Zr drier and baking the films at 190°C , the films dried within 90–120 min.

From Table IV, it can be seen that the films prepared from synthesized water-reducible resins were flexible, with excellent adhesion and high impact strength. The films also exhibited excellent water and acid resistances and good alkali resistance, as shown in Table V. Moreover, these properties tend to be improved with increasing amounts of acrylic copolymer, as was observed for alkali resistance. This indicates that acrylic copolymer can improve the water, acid, and alkali resistances of alkyds, thus confirming the advantage of adding acrylic copolymer to alkyd resins.

TABLE IV
Properties of the Films Prepared from Synthesized Water-Reducible Acrylic-Alkyd Resins

Type of alkyd resins	Flexibility (\varnothing , mm)	Adhesion	Impact strength (inch-pound)
20% acrylic	3	5B	160
25% acrylic	3	5B	160
30% acrylic	3	5B	160
35% acrylic	3	5B	160

TABLE V
Water, Acid, and Alkali Resistances of Films Prepared from Synthesized Water-Reducible Acrylic-Alkyd Resins

Type of alkyd resins	Water resistance ^a (h)	Acid resistance ^b (h)	Alkali resistance ^c (min)
20% acrylic	Excellent ^d	Excellent ^d	60
25% acrylic	Excellent ^d	Excellent ^d	150
30% acrylic	Excellent ^d	Excellent ^d	180
35% acrylic	Excellent ^d	Excellent ^d	210

^a Time detected when films exhibited blistering after immersing in water.

^b Time detected when films exhibited blistering after immersing in 5% H_2SO_4 .

^c Time detected when films exhibited blistering after immersing in 5% NaOH.

^d No change after immersing for 24 h.

CONCLUSION

Results reveal that water-reducible acrylic-alkyd resins, having excellent water and acid resistances and good alkali resistance, can be synthesized from esterification of monoglycerides prepared from modified palm oil and carboxy-functional acrylic copolymer, followed by neutralization of carboxyl groups with diethanolamine. Results suggest that this approach can be used to prepare an environmentally friendly binder from agricultural products such as palm oil.

The authors gratefully acknowledge Chulalongkorn University for financial, materials, and instruments support. We are also thankful to Bank of Thailand and Morakot Industries Co., Ltd. (Samutprakarn, Thailand) for materials support.

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