

Plasticization of Methylacrylamide Copolymers by Grafting onto a Styrene-Butadiene Backbone

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Synopsis

The development of a methylacrylamide-styrene copolymer into a product suitable for use as a general-purpose industrial or appliance enamel has been described; the choice of a suitable means of plasticization is emphasized. The incorporation of ethyl acrylate in the copolymer is expensive and was found relatively inefficient. Plasticization by blending the copolymer with tricresyl phosphate, butyl cyclohexyl phthalate, or dioctyl phthalate gave excessive thermoplasticity. Attempted plasticization by blending the copolymer with conformationally different macromolecules failed owing to incompatibility; this was overcome by reacting the macromolecules with the acrylic copolymer instead of blending: First, a butyl alcohol modified methylacrylamide-styrene copolymer was transesterified with cetyl alcohol and in a second synthesis, transesterified with coconut oil monoglyceride. Third, an acrylamide-styrene-acrylic acid copolymer was esterified by the same monoglyceride, methylolated, and then butylated. Finally, an acrylamide-styrene copolymer was copolymerized and grafted onto a styrene-butadiene copolymer. This latter type of plasticization, which should be a general and valuable method, was supplemented by plasticization from dioctyl phthalate and yielded, after heating, economical and durable films with good mechanical properties.

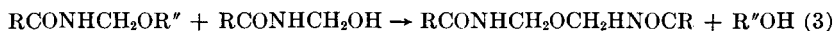
INTRODUCTION

In a previous paper,¹ we described the methylolation of acrylic (and vinyl) copolymers with formaldehyde, using basic catalysis. The present communication reports the systematic development of this type of copolymer into a product suitable for formulation as a general purpose industrial enamel or appliance enamel; numerous methods of plasticization are compared, and the results are of practical importance. To meet the requirements of these enamels, the polymers were synthesized with a view to achieving good film properties over a range of baking or crosslinking schedules (110-145°C./0.5 hr.) and acceptable durability to degradation by soap and detergent solutions; finally, the polymers had to be within the price range of alkyd-melamine formaldehyde condensate blends which, because of their cheapness, are widely employed in the general-purpose stoving enamel industry despite their relatively poor durabilities and low resistances to yellowing on overbaking, compared with acrylic enamels.

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DISCUSSION

The methylation, etherification, and crosslinking of amido substituted acrylic copolymers or monomers (usually acrylamide) are analogous to the reactions² of urea and melamine and may be represented by eqs. (1)–(4).



where R is the nonreactive portion of acrylic monomer or copolymer, R' = alkyl, and R'' = alkyl or H. Reaction (1) is both acid- and base-catalyzed. When alkanol solvents are present, etherification [eq. (2)] may take place, but only to an appreciable extent in the simultaneous presence of acid. In acidic environments and in contrast to basic, crosslinking, as represented by eqs. (3) and (4) is facilitated.

Our initial experiments were concerned with the effect of film properties of the degree of methylation and etherification prior to baking of the copolymers. Thus, an acrylamide-ethyl acrylate-styrene copolymer in butyl alcohol-xylene was preferentially methylated by formaldehyde

TABLE I
Evaluation of Films from Enamels (Overall Styrene:Acrylamide:Plasticizer Ratios of 76.5:8.5:15) after Heating at 140°C./0.5 hr.

Copolymer		Unpigmented films	Pigmented films		
Composition	Blended	Com- pat- ibility	Flex- ibility/ adhe- sion	Hardness	Gloss
A Styrene/acrylamide ^a / ethyl acrylate (76.5:8.5:15)	—	Good	4	Hard	75
B Styrene/acrylamide ^b / ethyl acrylate (76.5:8.5:15)	—	Good	4	Hard	85
C Styrene/acrylamide ^a (90:10)	Coconut oil alkyd	Poor	—	—	—
C Styrene/acrylamide ^a (90:10)	Dehydrated castor oil alkyd	Bad	—	—	—
C Styrene/acrylamide ^a (90:10)	Castor oil alkyd	Bad	—	—	—
C Styrene/acrylamide ^a (90:10)	Safflower oil alkyd	Bad	—	—	—
C Styrene/acrylamide ^a (90:10)	Methacrylated hydrogenated castor oil	Bad	—	—	—

(continued)

TABLE I (continued)

Copolymer		Unpigmented films	Pigmented films		
Composition	Blended	Com- pat- ibility	Flex- ibility/ adhe- sion	Hardness	Gloss
C Styrene/acrylamide ^a (90:10)	Coconut oil mono-glyceride	Bad	—	—	—
D Styrene/acrylamide ^b (90:10)	Coconut oil alkyd	Bad	—	—	—
D Styrene/acrylamide ^b (90:10)	Dehydrated castor oil alkyd	Bad	—	—	—
D Styrene/acrylamide ^b (90:10)	Castor oil alkyd	Bad	—	—	—
D Styrene/acrylamide ^b (90:10)	Safflower oil alkyd	Bad	—	—	—
D Styrene/acrylamide ^b (90:10)	Methacrylated hydrogenated castor oil alkyd	Bad	—	—	—
D Styrene/acrylamide ^b (90:10)	Coconut oil mono-glyceride	Bad	—	—	—
E Styrene/acrylamide ^b / cetyl alcohol (76.5:8.5:15)	—	Good	4	Hard	76
F Styrene/acrylamide ^b / coconut oil mono-glyceride (76.5:8.5:15)	—	Good	4	Hard	78
G Styrene/acrylamide ^b / acrylic acid/coconut oil monoglyceride (76.5:8.5:4:15)	—	Good	3	Very hard	75
D Styrene/acrylamide ^b (90:10)	Triresyl phosphate	Good	1	Soft ^c	92
D Styrene/acrylamide ^b (90:10)	Butyl cyclohexyl phthalate	Good	1	Soft ^c	92
D Styrene/acrylamide ^b (90:10)	Dioctyl phthalate	Good	1	Soft ^c	92
H 85 parts styrene/ acrylamide ^b (90: 10) grafted on 12.5 parts styrene/ butadiene	Dioctyl phthalate	Good	2	Very hard	80

^a Amido groups subsequently methylolated.

^b Amido groups subsequently methylolated and then etherified with butyl alcohol.

^c Films thermoplastic; determinations observed at 20°C.

using triethylamine catalyst. This copolymer, designated copolymer A, was then etherified by the butyl alcohol solvent as the result of acidification of the medium with excess maleic anhydride which acts as an acid by reacting with the butyl alcohol to form the monobutyl ester. Crosslinking between macromolecules [reactions (3) and (4)], is probably slight in the presence of the excess butyl alcohol solvent. This latter copolymer was designated copolymer B. As expected, the infrared spectrum of copolymer A had maxima near 3300 and 1040 cm^{-1} but only slight absorption near 1080 cm^{-1} , which indicated methylolation without etherification, whereas copolymer B had relatively strong C—O— stretching vibration absorption at 1080 cm^{-1} and weaker absorption at 1040 cm^{-1} , indicating methylolation with etherification. Both copolymers were pigmented with rutile titanium dioxide and individually self-condensed by heating at 140°C. for 0.5 hr. to form glossy, rather brittle, and solvent-resistant films. However, the gloss (Table I) of copolymer B was higher than that of copolymer A.

Obviously, the ethyl acrylate in these instances was not very effectively plasticizing the films. Further increase in the ethyl acrylate content would have adversely affected the price of the copolymers and, therefore, a different means of plasticization was sought. Plasticization by blending with alkyd or fatty acid monoglyceride was planned for two reasons. First, the conformations of these macromolecules should differ considerably from the more ordered acrylic copolymer molecules and hence, when blended, produce more disorder and thus plasticization,^{3a} than had been achieved by the incorporation of ethyl acrylate. Second, the elimination of the relatively expensive ethyl acrylate plasticizer brought the resulting enamels in the price range of existing products.

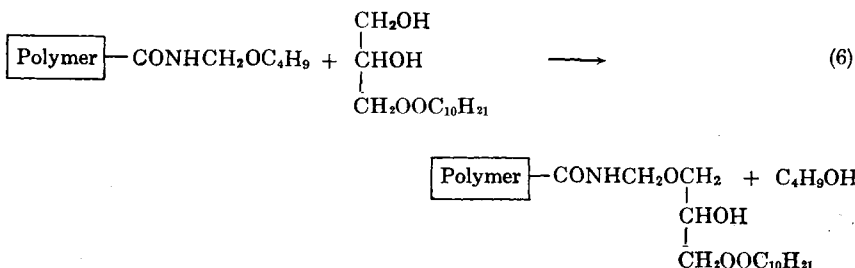
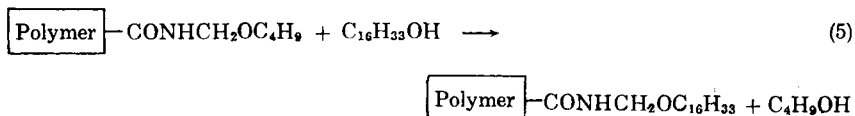
The following experiments yielded a guide to plasticization by these means and to the effect of the modification of methylolamide copolymers by etherification. A monoglyceride, methacrylated alkyd, and a range of alkyds (Table I), chosen because they were derived from oils with relatively low content of double bonds and which should, therefore, give a minimum degree of yellowing on heating, were selected for plasticizing a butylated methylolacrylamide-styrene copolymer, designated copolymer D. In the formulations the ratio of plasticizer:acrylamide:styrene was equal to that used in A and B. However, it can be seen from Table I that the alkyds and monoglyceride which all contain strongly polar groups, were incompatible with the relatively nonpolar copolymer D. A more polar copolymer, C, of identical composition to D except that the methylolamide groups were nonetherified, showed some increased compatibility with the coconut oil-glyceryl phthalate alkyd, but the incompatibility was still of an order which discouraged pursuit of plasticization by blending with alkyd or monoglyceride.

The mixing process⁴ of a ternary system of two polymers and a mutual solvent is governed by the thermodynamic equation: $\Delta G = \Delta H - T \Delta S$ where T is the absolute temperature; ΔH is the change in internal heat

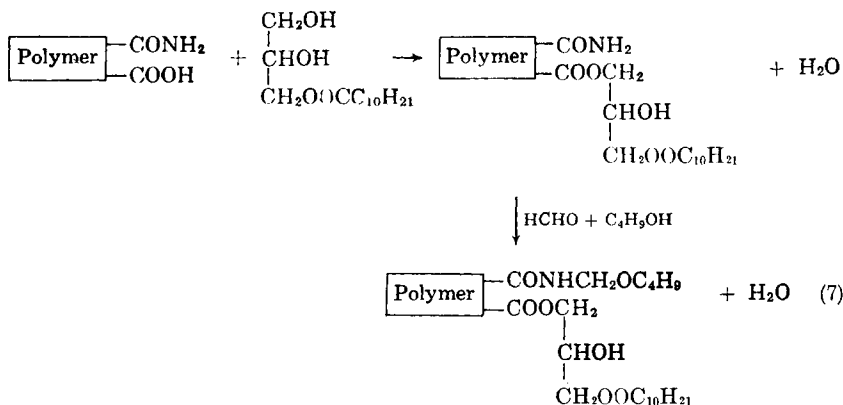
of the system and which results from intermolecular interactions during mixing; ΔS is the entropy change during mixing, and ΔG is the free energy change during mixing. With macromolecules, ΔS will be slight, usually small and positive. Most polymers mix with accompanying heat absorption (ΔH , positive) and this term invariably outweighs the term $T\Delta S$ owing to the small magnitude of ΔS . As a consequence, ΔG is positive, and incompatibility between macromolecules is most often observed.⁴ One exception which is to be expected is during the mixing of polymers containing polar groups which react to give negative ΔH 's and hence negative free energy change during mixing.

Thus, it was hoped that plasticization could be achieved, and at the same time, the problem of incompatibility overcome, if the monoglyceride (or a long chain alcohol) were reacted instead of blended with the methylolacrylamide-styrene copolymer. Three general types of syntheses were assessed: first, a butyl alcohol-modified methylol-acrylamide-styrene copolymer was transesterified (copolymer E) with cetyl alcohol; in a second synthesis (copolymer F) the copolymer was transesterified with coconut oil monoglyceride; third, an acrylamide-styrene-acrylic acid copolymer was esterified by the same monoglyceride and then methylolated and etherified with butyl alcohol solvent (copolymer G). In all cases, the styrene:acrylamide:plasticizer ratio (76.5:8.5:15), was kept the same as that in copolymers A, B, C, and D. The syntheses succeeded in giving, after baking, compatible, solvent-resistant films but unfortunately, the plasticizing effect of the monoglyceride (and alcohol) was reduced to an impractical level.

The reactions involved in the syntheses of the polymers E, F, and G are represented by eqs. (5)–(7).



Consequently, another means of plasticization of methylolacrylamide copolymers was evaluated. Copolymer D was blended, so as to maintain the previous styrene:acrylamide:plasticizer ratio, in turn, with tricresyl phosphate, butyl cyclohexyl phthalate, and dioctyl phthalate. After heat-



ing at 140°C./0.5 hr. (Table I), the films were clear, solvent-resistant, and flexible. Resistances to yellowing on overbake were good. However, the films were noticeably thermoplastic. (This result is in harmony with the view that these conventional "external" plasticizers function by forming a suspension or a partial solution of the polymeric molecules^{3b}).

To summarize, four methods of plasticization have been investigated: (a) copolymerization with a plasticizing monomer; (b) blending with an alkyd or monoglyceride; (c) synthesis of a monoglyceride or long-chain alcohol into the copolymer; (d) blending with conventional "external" plasticizers. During evaluations of (d) it was found that lower plasticizer levels gave acceptable thermoplasticity over the range 0–100°C. but excessive brittleness. Thus, it appeared that this means of plasticization should be supplemented by another. An unusual method was considered and gave very rewarding results. It was decided to graft onto a styrene–butadiene copolymer (12.5 parts), a mixture (85 parts) of acrylamide and styrene (10:90) and then subsequently methylolate and butylate. At the same time, it was recognized that this type of plasticization, being devoid of hydrolyzable groups, should lead to high soap durability. The resulting polymer (copolymer H) was blended with dioctyl phthalate (2.5 parts), pigmented, sprayed, and heated at 140°C./0.5 hr. The results of its evaluations were, on the whole, good (Table I) and an enamel developed upon this formula compared favorably with a commercial appliance enamel and a general-purpose industrial enamel (Table II).

In the past, it has not been a general practice to graft acrylic copolymers and monomers onto polymers of styrene–butadiene, specifically and exclusively to achieve plasticization. We believe this means of plasticization shows considerable promise in a wide range of surface coatings. The virtues of enamels of this type are that they are equivalently priced to cheap alkyd–nitrogen resin blends but, being acrylic, have their superior resistances to yellowing and durabilities to soap and detergent solutions; moreover the method of plasticization is efficient and is not subject to the frequent incompatibility associated with the blending of macromolecules.

TABLE II
Comparison of Experimental Enamel with Commercial Products

	Gloss ^a	Flex- ibility/ adhesion ^a	Gloss ^b	Yellowing ^b	Flexi- bility/ adhe- sion ^b	Durabilities, ^b hr.	
						Soap	De- ter- gent
Appliance enamel	90	1	82	Very slight	1	1	8
General-purpose industrial enamel	90	3	75	Mod- erate	1	1	3
Experimental enamel (styrene/butadiene grafted methylol- acrylamide copolymer	86	2	82	Nil	1	300	60

^a After heating 0.5 hr. at 110°C.

^b After heating 0.5 hr. at 145°C.

EXPERIMENTAL

General

The general methods which were used to determine purity of monomers, solids, infrared spectra, compatibility of enamels, solubility of films in butyl acetate, and durabilities in soap and detergent solutions have been described previously.¹

Unpigmented films were formed on glass by a 0.0042 in. doctor blade. Pigmented enamels were sprayed such that the dry film thickness was 0.0015 in. when determined with an elcometer; degreased steel substrates were used in all cases except for the comparisons with the commercial appliance enamel (Table II) when 6 in. × 4 in. phosphated steel panels were employed.

Gloss and hardness were determined by standard methods.⁵ Flexibility/adhesion⁵ was observed after spraying films to 0.0015 in. dry thickness and then blending over a 0.25 in. mandrel. The following ratings were used: no cracking at bend = 1; slight cracking at bend but film not lifted from panel = 2; slight cracking at bend and film lifted from panel = 3; extensive cracking and film lifted from panel = 4; film completely lifted from panel = 5.

The alkyd resins were prepared by conventional methods; the constants and compositions (mole ratios) are given in Table III.

The appliance enamel was a 60:40 (solids basis) blend of the dehydrated castor oil alkyd and a melamine-formaldehyde condensate. The general-purpose industrial enamel was a 70:30 blend of the castor oil alkyd and the melamine-formaldehyde condensate. The melamine-formaldehyde resin

TABLE III

	Viscosity, poise	Acid value	Solids, %
Dehydrated castor oil-glycerol-phthalic anhydride (1:4.8:4.5)	11	10	50
Castor oil-glycerol-phthalic anhydride (1:3.79:4.61)	8	20	50
Coconut oil-glycerol-phthalic anhydride (1:5.06:6.12)	18	25	55
Safflower oil-pentaerythritol-phthalic anhydride (1:3.33:3.32)	30	6	53

was that reported earlier.¹ The styrene-butadiene was supplied by the Enjay Company Inc., under the trade name Buton 100. The methacrylated alkyd⁶ had the composition (on a weight basis) of methyl methacrylate-hydrogenated castor oil-glycerol-phthalic anhydride (28.6:36.3:11.3:23.8).

Preparation of Copolymers

Copolymer A. Acrylamide (85 g.), hydroquinone (128 mg.), and butyl alcohol (666 g.) were brought slowly to 90°C. and then filtered. After cooling, styrene (765 g.), ethyl acrylate (150 g.), xylene (333 g.), and cumene hydroperoxide (10 g.) were added and the solution refluxed for 5 hr., more catalyst (10 g.) being added after the 2 and 4 hr. The next day, paraformaldehyde (180 g.) and triethylamine solution (40 g.; 30% solution in xylene) were added to the solution to pH 9.4. After refluxing for 2 hr., solvent (333 g.) was distilled and replaced by xylene (333 g.). Solids were 49%. The infrared spectrum of the copolymer had maxima near 3300 (methylolamido), 1730 (ester), 1040 (methylol), 770, and 700 cm.⁻¹ (aromatic).

Copolymer B. Solvent and excess triethylamine (175 g.) from copolymer A (1 kg.; total weight including solvent) were distilled and replaced by butyl alcohol (175 g.). After acidification with maleic anhydride (5 g.) to pH 3.5, the solution was refluxed for 1 hr. The copolymer showed absorption near 1080 cm.⁻¹ (butyl methylol). Solids were 49%.

Copolymer C. This was prepared similarly to copolymer A from acrylamide (100 g.) and styrene (900 g.). The resulting copolymer had solids of 48% and infrared absorption maxima near 3300, 1040, 770, and 700 cm.⁻¹.

Copolymer D. The copolymer, solids 49%, infrared maxima near 3300, 1080, 770, and 700 cm.⁻¹, was prepared by the butylation of copolymer C in an analogous manner to the conversion of copolymer A to B.

Copolymer E. Cetyl alcohol (150 g.) was added to a copolymer, prepared in an analogous way to copolymer A from acrylamide (85 g.), styrene (765 g.), butyl alcohol (666 g.), and xylene (333 g.). Solvent (300 g.) was distilled and simultaneously replaced with xylene (300 g.); then the

solution was refluxed for 5 hr. A solids determination gave 48%, and the copolymer had infrared maxima near 3300 and 1080 cm.^{-1} .

Coconut Oil Monoglyceride. Lead naphthenate solution (0.5 g.; 14% metal) was added to coconut oil (400 g.) and glycerol (100 g.) at 150°C. The temperature was raised to 240–250°C. and maintained for 0.5 hr. An aliquot (1 part) was cooled to room temperature and gave a clear solution in ethyl alcohol (2 parts).

Copolymer F. The copolymer, solids 49%, infrared maxima near 3300, 1740, and 1080 cm.^{-1} , was prepared in an identical manner to copolymer E except coconut oil monoglyceride was substituted for cetyl alcohol.

Copolymer G. In the usual manner, a copolymer was synthesized from acrylamide (85 g.), acrylic acid (40 g.), and styrene (765 g.) in xylene (333 g.) and butyl alcohol (666 g.). Solvent (1 kg.) was distilled and replaced simultaneously with xylene (1 kg.). Coconut oil monoglyceride (150 g.) was added to the hot solution and solvent was distilled until the internal temperature was ca. 215°C. After maintaining at this temperature for 1 hr., the solution was cooled and diluted with xylene (666 g.) and butyl alcohol (333 g.). Upon cooling to ca. 35°C., paraformaldehyde (180 g.) and maleic anhydride (4 g.) were added and the whole refluxed for 3 hr. The copolymer had infrared absorption near 3300, 1730, and 1080 cm.^{-1} ; solids were 48%.

Copolymer H. Acrylamide (85 g.), hydroquinone (128 mg.), and butyl alcohol (666 g.) were brought slowly to 90°C. and filtered. After cooling, styrene (765 g.) and cumene hydroperoxide (30 g.) were added and the resulting solution added over 2 hr. to a refluxing solution of Buton 100 (125 g.) in xylene (333 g.). Reflux was continued for 3 hr., and then the copolymer was methylolated and butylated in the usual way. Solids were 48%; the copolymer had maxima in the infrared near 3300 and 1080 cm.^{-1} .

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Résumé

On décrit une méthode de développement du copolymère de méthylolacrylamide-styrène pour en faire un polymère susceptible d'être employé comme émail utilisable soit comme produit industriel d'usage général soit pour des emplois particuliers. On

s'attache surtout à décrire le choix d'agents plastifiants recommandables. L'incorporation d'acrylate diéthyle au copolymère est coûteux et peu efficace. Lorsqu'on plastifie le polymère avec du phosphate tricrésylique, du phtalate de butyle et de cyclohexyle ou de dioctyle, on obtient un produit qui possède une trop grande thermoplasticité. Le mélange physique du copolymère avec des polymères de structure différente n'est pas possible, les polymères étant incompatibles. On a surmonté cette difficulté en faisant réagir chimiquement les polymères en présence: en premier lieu un copolymère de méthylolacrylamide, modifié par l'alcool butylique est transestérifié par l'alcool cétylique et ensuite, dans une seconde synthèse, transestérifié par l'huile de noix de coco monoglycérinée. En troisième lieu, un copolymère acide acrylique styrène a été estérifié par le même monoglycéride, méthylolé et butylé. Enfin, un copolymère styrène-acrylamide était copolymérisé et greffé sur un copolymère styrène-butadiène. A cette dernière méthode de plastification, on ajoute, ce qui reste une méthode générale et précieuse, une plastification au phtalate de dioctyle. On obtient un produit qui, après chauffage, fournit des films économiques et résistants possédant de bonnes propriétés mécaniques.

Zusammenfassung

Es wird die Entwicklung eines Methylolacrylamid-Styrol-Copolymeren zu einem in Industrie und anderen Anwendungsgebieten allgemein verwendbaren Email beschrieben. Die Wahl einer geeigneten Weichmachungsmethode wird hervorgehoben. Die Einführung von Äthylacrylat in das Copolymere ist teuer und relativ unwirksam. Die Weichmachung des Polymeren mit Trikresylphosphat, Butylcyclohexylphthalate oder Dioctylphthalat führte zu übermässiger Thermoplastizität. Der Versuch einer Weichmachung durch Mischen des Copolymeren mit Makromolekülen anderer Konformation schlug wegen deren Unverträglichkeit fehl. Diese Schwierigkeit wurde dadurch überwunden, dass man statt des Mischens die Makromoleküle mit dem Acrylcopolymeren reagieren liess. Ein mit Butylalkohol modifiziertes Methylolacrylamid-Styrol-Copolymeres wurde einerseits mit Cetylalkohol und andererseits mit Kokosnussöl-"Monoglycerid" transveräthert. Ferner wurde ein Acrylamid-Styrol-Acrylsäure-Copolymeres mit dem gleichen "Monoglycerid" verestert, methyliert und dann butyliert. Schliesslich wurde ein Acrylamid-Styrol-Copolymeres copolymerisiert und auf ein Styrol-Butadien-Copolymeres aufgefropft. Diese letzte Art der Weichmachung, die allgemein und gut anwendbar sein dürfte, wurde durch Weichmachung mit Dioctylphthalat ergänzt und ergab nach der Hitzebehandlung wirtschaftliche und dauerhafte Filme mit guten mechanischen Eigenschaften.

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