

Thiuram Vulcanization of Natural Rubber in the Presence of Hydrofuramide and Ethanolamines

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Synopsis

Influence of hydrofuramide and ethanolamines on efficient vulcanization (EV), semi-EV, and conventional sulfur vulcanization accelerated by tetramethyl thiuram disulfide is reported. In the case of thiuram vulcanization, the amines increase the cure rate but reduce the crosslink density. The interaction of tetramethyl thiuram disulfide with amines has been studied. The amines interact with thiuram disulfide (TMTD) giving rise to the formation of gaseous products. Thermogravimetric analysis shows weight loss of about 50% in case of TMTD-ethanolamine system and 25% in case of TMTD-hydrofuramide system. Gas chromatographic studies of the gaseous products indicate that it consists mainly of H_2S . The other constituents in the gaseous product are CO_2 and a thiol. A possible reaction based on these observations to account for decrease in crosslink density in thiuram vulcanization caused by amines is reported.

INTRODUCTION

In an earlier communication¹ it has been reported that hydrofuramide (a reaction product of furfural and ammonia), although it increases the cure rate of thiuram vulcanization, causes decrease in crosslink density in the resulting vulcanizate. An extension of this work with some amines such as triethanol amine (TEA), diethanolamine (DEA), hexamine, and ammonium bicarbonate, etc., gave similar results. It was established that the general characteristic of amino compounds is to reduce the crosslink density in the thiuram vulcanization system. It has also been reported² that this influence of amines on thiuram vulcanization is related to their basicity. Aliphatic amines being stronger bases improve the cure rate significantly, whereas aniline and its derivatives being weaker do not increase the cure rate. Also, the stronger the base, the more the decrease in crosslink density. However, it has been reported¹ that hydrofuramide does not decrease the crosslink density in a sulfur cured system accelerated by tetramethylthiuram disulfide (TMTD).

In the present paper the possible reason for the decrease in crosslink density caused by amines in thiuram vulcanization system has been discussed.

EXPERIMENTAL

Hydrofuramide was freshly prepared in the laboratory by reacting furfural with ammonia gas.³ It was recrystallized from peroxide-free diethylether. The physicochemical parameters of hydrofuramide have been described elsewhere.¹ TMTD was supplied by Bayer (India) Ltd. Sulfur used was 99.9% pure. The purity of other chemicals was the same as described earlier.^{1,2,4}

Compounding and Curing

Mixing of the ingredients was carried out in a laboratory-size two-roll mill (33 × 15 cm) with a friction ratio of 1:1.4 as described earlier.^{1,2,4} Cure characteristics of the compounds were studied with the help of a Monsanto Rheometer (Model R-100) fitted with a microdie.

Thermogravimetric Analysis

Mixtures of TMTD and the amines on heating at the vulcanization temperature (150°C) were found to evolve some gaseous products with a characteristic smell. The interaction between TMTD and the amines was followed by measuring the mass loss due to the escape of gaseous products using the thermogravimetric apparatus. Mixtures of TMTD and the amines in the same ratio as the one used in the vulcanization system^{1,2} (4 g TMTD/0.01 mole amine) were prepared. Thermograms were recorded with the sample maintained at 150°C using a temperature controller. From the difference in initial and final mass the percent loss was calculated.

Gas Chromatographic Analysis

The gaseous products evolved on reacting TMTD and amines were analyzed gas chromatographically (Amil Mark II, dual column) using a Poropak Q column at 110°C and hydrogen as the carrier gas. The air peak was taken as the arbitrary standard to determine the relative retention time of the constituents of the gaseous mixture. The retention times of some compounds such as H₂S, NH₃, (CH₃)₂NH, CO₂, and CS₂ which may be formed during the reaction, were also determined by injecting the standards.

RESULTS AND DISCUSSIONS

Rheometric Study

It can be seen from Figure 1 that in a thiuram vulcanization system (in absence of elemental sulfur) the cure rate increases progressively with increasing levels of hydrofuramide. The curve more or less follows a straight-line pattern beyond 1.0 phr of hydrofuramide. It is also apparent that the maximum torque (t_{max}) which is proportional to crosslink density, decreases with increasing level of hydrofuramide.

The influence of hydrofuramide on efficient, semiefficient, and conventional TMTD accelerated vulcanization systems is given in Table I. It can be observed from Table I that in a low sulfur (TMTD 4.0 phr, sulfur 0.3 phr) system, 2.0 phr of hydrofuramide brings about 200% increase in cure rate. As the level of TMTD decreases and sulfur increases, the influence of hydrofuramide on cure rate becomes much less. However, it is interesting to note that in case of low sulfur system torque modulus decreases by the presence of hydrofuramide and as the proportion of sulfur increases and TMTD decreases (that is in semiefficient type of system) the decrease in torque modulus caused by hydrofuramide becomes less significant. When the curing system is TMTD 1.75 phr and sulfur 1.25 phr

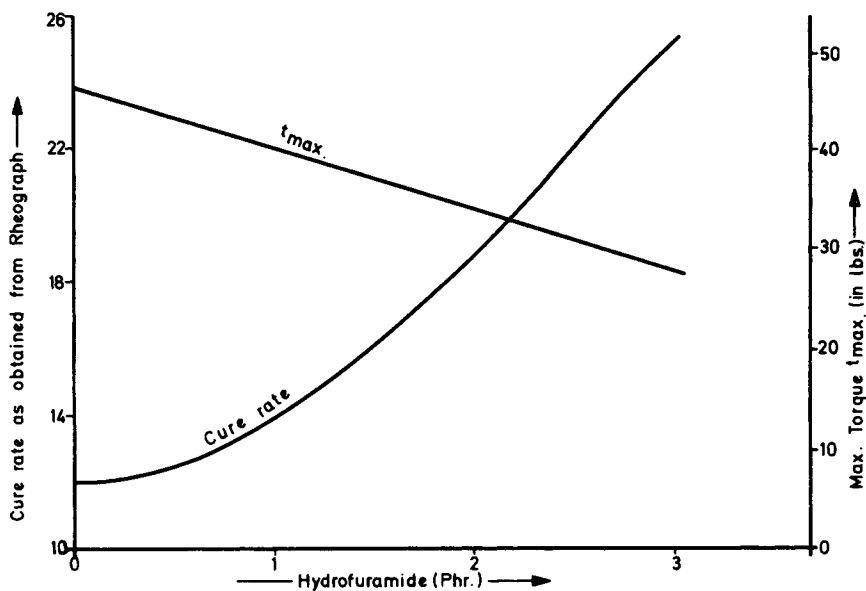


Fig. 1. Effect of hydrofuramide concentration on cure rate and t_{max} . Base formula: NR—100; ZnO—5, St. acid—2, TMTD—4.

(compounds 6 and 7), the t_{max} , in the presence and absence of hydrofuramide, is the same. At a still higher level of sulfur and lower level of TMTD (compounds 8 and 9) presence of hydrofuramide, instead of decreasing, causes an increase in t_{max} . The influence of other amines like TEA, hexamine, etc., on efficient, semiefficient, and conventional system was found to follow similar trend as hydrofuramide. This indicates that the amino compounds cause a decrease in crosslink density and hence torque modulus, when TMTD is the sole vulcanizing agent. The influence of hydrofuramide and ethanol amines in other sulfur donor system was also investigated. When benzothiazyl-dithiomorfolide (BDTM), a sulfenamide accelerator cum sulfur donor⁵ is used as a sole vulcanizing agent (in absence of elemental sulfur) the presence of hydrofuramide and ethanolamines causes reduction in crosslink density and torque modulus (t_{max}) and increases cure rate as in thiuram vulcanization system. This leads to the conclusion that amines reduce crosslink density and increase cure rate in sulfur donor system.

The increase in cure rate caused by hydrofuramide could probably be explained on the basis of ionic mechanism of thiuram vulcanization in presence of zinc oxide as proposed by Bateman and co-workers,⁶ and also by Manik and Banerjee⁷:

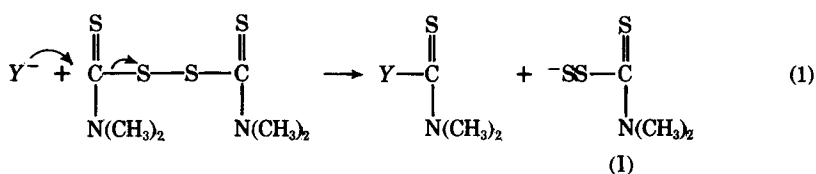
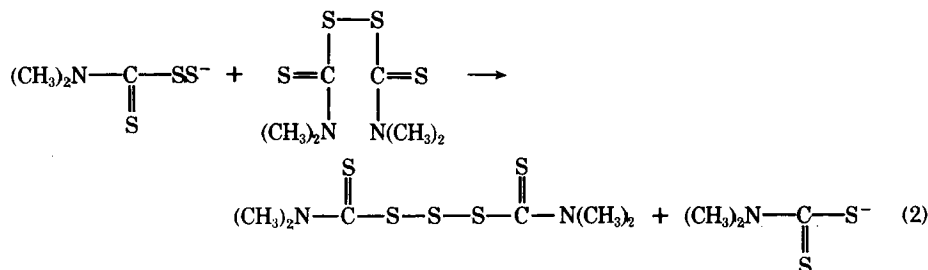


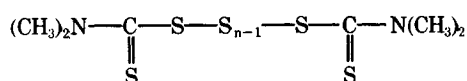
TABLE I
Influence of Hydrofuramide on Cure Characteristics of EV, Semi-EV and Conventional Sulfur Vulcanization.

Base formula	100												
Natural Rubber	5												
Zinc oxide	2												
Stearic acid	1												
Compound	4.0	4.0	2.5	2.5	1.75	1.75	1.0	1.0	1.0	1.0	1.0	0.5	10
TMTD	0.3	0.3	1.0	1.0	1.25	1.25	1.75	1.75	1.75	1.75	2.25	2.25	2.25
Sulfur	—	2.0	—	2.0	—	2.0	—	—	—	—	—	—	2.0
Hydrofuramide													
Rheometric parameters													
Maximum torque (in lb)	57.8	49.5	60.0	57.0	58.1	58.0	56.5	62.2	62.2	58.4	58.4	64.4	64.4
Cure rate	10.29	32.78	25.84	40.0	44.65	54.05	42.55	45.20	45.20	45.95	45.95	59.44	59.44
Optimum cure time (min)	12.4	5.37	6.45	4.65	6.0	4.75	5.15	4.04	4.04	5.1	5.1	4.23	4.23

where Y^- is a basic oxianion. The per thio anion (I) then preferentially attacks a disulfide sulfur atom of TMTD to give tetramethyl thiuram trisulfide:



Further attack of Y^- on trisulfide leads to the formation of tetrasulfide and the process goes on to the formation of a still higher polysulfide of the general formula



which, in absence of possibility for other reactions, would finally eliminate active elemental sulfur. Bateman et al. proposed a stoichiometric equation putting Y^- as ZnO . Presence of hydrofuramide or other amino compounds in the thiuram vulcanization system is likely to increase the concentration of Y^- (anion) and hence increase the cure rate. This also explains the role of basicity of amines on the cure rate of thiuram vulcanization system as reported earlier.² Higher the pKa value of amine, higher is the activity of Y^- and hence higher cure rate.

Thermogravimetric Analysis

Thermogravimetric analysis confirms that interaction of TMTD and amines results in formation of some gaseous products. It can be seen from the thermograms (Fig. 2) that TMTD and amines when heated separately do not show any mass loss at the reaction temperature. However, when mixtures of the amines and TMTD are heated a considerable mass loss is observed. Thermograms show sharp mass losses at 110°C for TMTD-DEA, at 125°C for TMTD-TEA, and at 140°C for TMTD-hydrofuramide mixtures, the last one being comparatively lower than the other two. The sharp mass losses shown by mixtures evidently suggest that TMTD and amines take part in some chemical reaction at a temperature above 100°C resulting in gaseous products. This interaction could probably account for the decrease in crosslink density in thiuram vulcanization by making part of TMTD nonavailable for the vulcanization reaction.

Gas Chromatographic Analysis

Chromatograms of the gases evolved from TMTD-DEA and TMTD-TEA mixtures are shown in Figures 3 and 4, respectively. The former shows two sharp

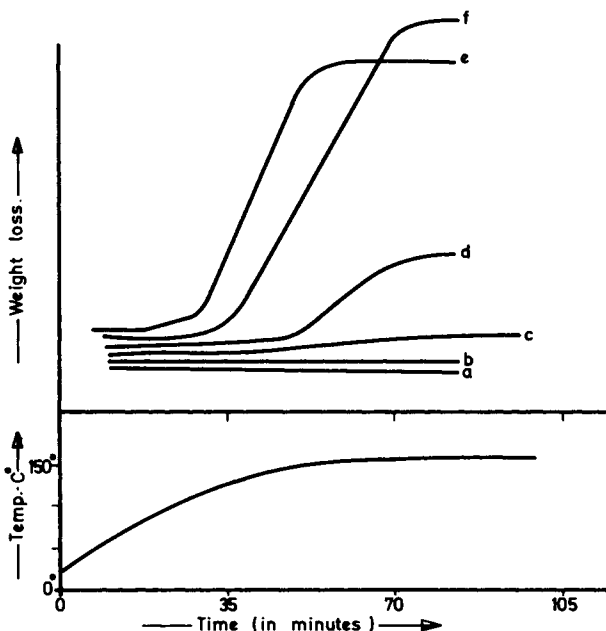


Fig. 2. Thermograms for (a) DEA, (b) TEA, (c) TMTD (1% weight loss), (d) TMTD-HF (26% weight loss), (e) TMTD-DEA (49% weight loss), and (f) TMTD-TEA (58% weight loss) systems (schematic).

peaks and one very small peak, and latter shows three sharp peaks apart from the air peak. Comparison of the retention times with standards showed that the major peak is of H_2S . In all the cases the gaseous mixture, when analyzed at regular intervals during the reaction, showed that the peak corresponding to H_2S is initially small and then becomes prominent and remains so during the course of the reaction. This shows that H_2S is the major product in the gaseous mixture produced by interaction of TMTD and amines. Another small peak corresponds to carbon dioxide. The identity of the other peak could not be established conclusively and is under study. In the case of TMTD-hydrofuramide system the gaseous product also consists chiefly of hydrogen sulfide.

Presence of a mercaptan vaporizing around 150°C seems likely from the odor of the gases. This is confirmed by the observation that the gaseous mixture, after passing successively through copper sulfate solution (to ensure complete removal of H_2S), when passed through solution of mercuric nitrate, gave a white precipitate characteristic of mercuric mercaptide. These observations suggest that the other constituent in the gaseous mixture could probably be a volatile thiol, which possibly accounts for the other peak.

Since H_2S is the major product in the gaseous mixture produced from TMTD-amine system, it seems logical that formation of H_2S could probably account for the major side reaction responsible for the decrease in crosslink density in thiuram vulcanization system. As reported earlier,² since the basicity is related to the extent of decrease in crosslink density, it is likely that the reaction of acidic accelerator TMTD with the basic amine first takes place.^{2,8} A typical

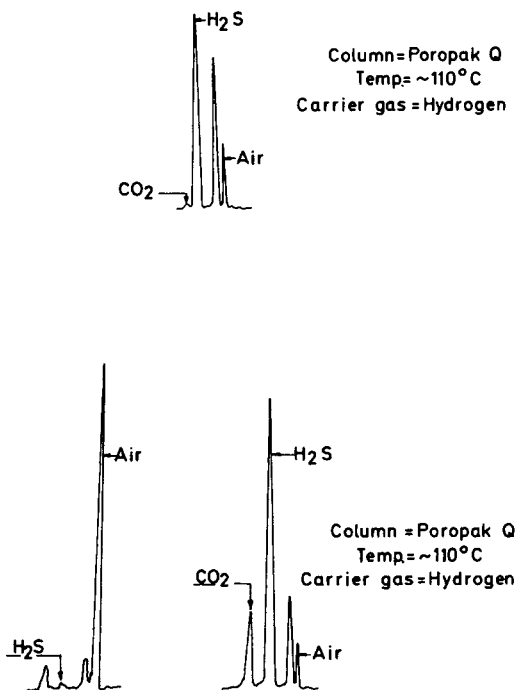
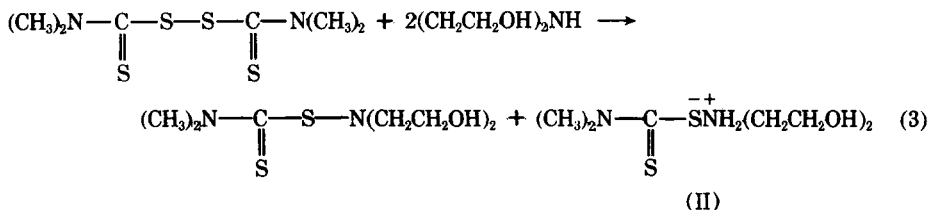
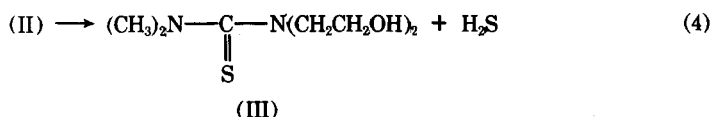


Fig. 3. (A) Chromatogram of the gases evolved from TMTD-DEA system on heating. (B) Chromatograms of the gases evolved from TMTD-TEA system on heating (a) initially and (b) after ca. 10 min.

reaction with DEA is given below:

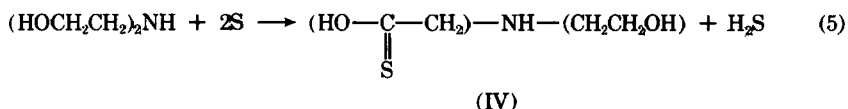


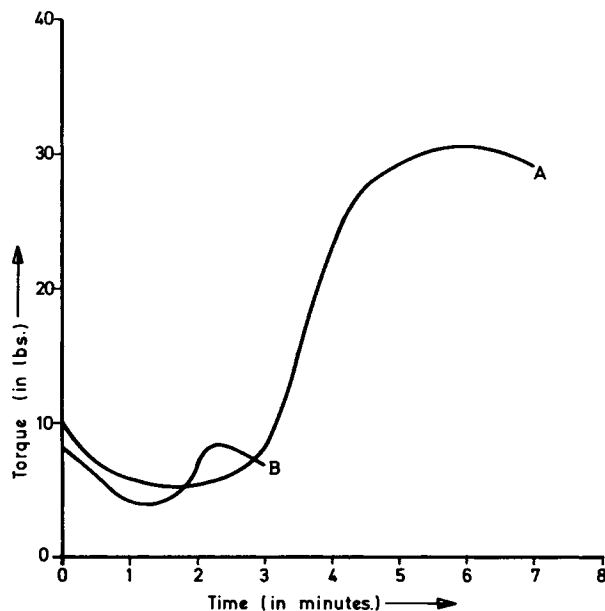
Compound II then liberates H₂S as follows:



Similar reaction schemes can be proposed for other amines also.

Hydrogen sulfide can also be produced by thermal reaction of active sulfur (formed by decomposition of tetramethyl thiuram trisulfide or from the polysulfide as proposed by Bateman) with nitrogen, containing bases^{5,7,9,10} as follows:

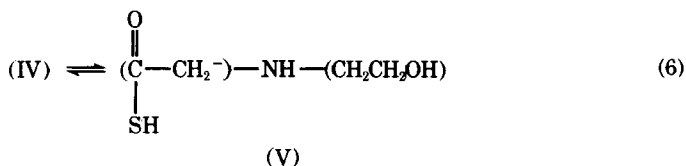




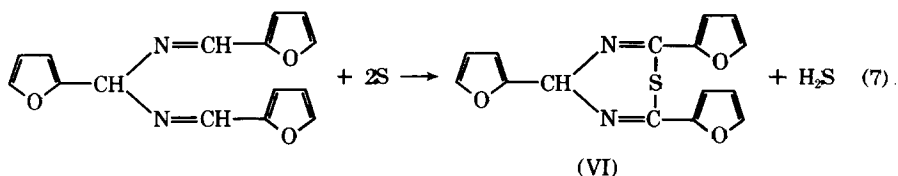
Effect of hydrofuramide on thiuram Vulcanization.
(in absence of Zinc oxide and elemental sulfur)

Fig. 4. Effect of hydrofuramide on thiuram vulcanization (in the absence of zinc oxide and elemental sulfur). Base formula: NR-100; TMTD-6.0. Curve A—no hydrofuramide; curve B—1.5 phr hydrofuramide. Rheograph at 160°C; arc 3°.

Compound IV can also exist in another form:



This is supported by IR spectra of the reaction product of TMTD and amine which shows a band around 1750 $^{\circ}$ cm $^{-1}$ which is the characteristic of a carbonyl group. In case of hydrofuramide the reaction is as follows:



In fact, when hydrofuramide was heated with elemental sulfur, H₂S was found to evolve which supports eqs. (5) and (7). Also determination of total and free sulfur in the reaction product of hydrofuramide and sulfur showed that 14% sulfur is chemically bound with hydrofuramide. (Theoretical value corresponding to compound VI is 12%.) IR spectra of the reaction product of hy-

dromamide and sulfur also shows a band around 850 cm^{-1} corresponding to C-S linkage. All these observations support formation of compound VI. The mixture of BDTM and amines on heating also results in a gaseous product consisting chiefly of hydrogen sulfide. This observation supports the view that amines scavenge the active sulfur from sulfur donor and results in formation of H_2S [as shown in eqs. (5) and (7)].

Equations (3), (4), (5), and (7) describe probable reactions which result in the formation of H_2S . Formation of H_2S according to eq. (4) converts TMTD into monosulfides which are no longer sulfur donors and cannot contribute to crosslink formation in the thiuram vulcanization (in absence of elemental sulfur). Formation of H_2S according to eqs. (5) and (7) is at the expense of active S (produced from TMTD) which is the actual vulcanizing agent in thiuram vulcanization.

Thus, formation of H_2S either according to eqs. (4) or (5) and (7) is only at the expense of actual curing agent in thiuram vulcanization and hence chemical reactions (4), (5), and (7) are responsible for the decrease in crosslink density in thiuram vulcanization.

Formation of H_2S according to eqs. (5) and (7) also accounts for the induction period in H_2S liberation (which probably corresponds to the time of liberation of sulfur from sulfur donor) as observed in chromatograms. Comparatively lower weight loss in the case of TMTD-hydrofuramide system could probably be due to the fact that hydrofuramide arrests some H_2S forming the polythiofurfural-type compound.¹¹ It becomes apparent from Figure 4 that presence of hydrofuramide practically prevents vulcanization by thiuram disulfide in absence of zinc oxide. Vulcanization by thiuram disulfide in absence of zinc oxide is known to follow radical mechanism by S^\cdot radical produced from thiuram disulfide or from trisulfide (produced by disproportionate reaction from TMTD to mono and trisulfide) as suggested by Craig et al.¹² Thus prevention of vulcanization by TMTD (in absence of zinc oxide) caused by hydrofuramide is due to scavenging of S^\cdot radical by amine probably according to eq. (7).

While crosslink density of thiuram vulcanization in presence of zinc oxide is reduced by hydrofuramide, in absence of zinc oxide, vulcanization with TMTD is practically prevented by hydrofuramide. This leads to the conclusion that S^\cdot radical produced from TMTD (in absence of zinc oxide) requires less energy to react with hydrofuramide in comparison with the energy required for abstracting H atom from isoprene unit. Active sulfur produced (from polysulfide as proposed by Bateman⁶) in thiuram vulcanization system in presence of zinc oxide is probably much more active in comparison to S^\cdot radicals produced from TMTD in absence of zinc oxide and hence active sulfur produced in thiuram vulcanization system (in presence of zinc oxide) react with isoprene unit (which is present in abundance) in addition to reacting with hydrofuramide and thus vulcanization is not totally prevented although crosslink density is decreased.

In the sulfur vulcanization system accelerated by TMTD, concentration of TMTD is less and hence according to the law of mass action, chemical reactions as shown in eqs. (3), (5), and (7) will be minimum. Besides, if an ammonium salt is produced during vulcanization in accordance with eq. (3) it can act as an ultraaccelerator in the sulfur vulcanization system. This explains why in the sulfur vulcanization system accelerated by TMTD (compounds 7 and 9 in Table I) amines do not decrease the crosslink density.

CONCLUSION

The amines influence thiuram vulcanization in an interesting manner. While the cure rate of thiuram vulcanization is increased by presence of amines, crosslink density is decreased. The decrease in crosslink density is due to some interaction of TMTD and amines resulting in some side reaction and thus making a part of TMTD not available for vulcanization reaction. A mechanistic scheme is proposed to explain the role of amines in increasing the cure rate of thiuram vulcanization.

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