

## SUPPRESSION OF REACTIVITY CHANGES IN Poly bd® R-45M RESIN

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## ABSTRACT

Poly bd R-45M resin, a hydroxyl terminated homopolymer of 1,3-butadiene, is a primary component in the binder for many solid propellant systems. The aging characteristics of this resin are such that its rate of reactivity with an isocyanate may increase during storage for prolonged time periods at ambient temperatures. As a result, the pot lives of propellant mixtures prepared from the same lot of Poly bd R-45M resin may differ significantly over a period of months. Under certain processing conditions, this reactivity difference may pose problems for the formulator. The addition of triphenylphosphine to the Poly bd R-45M resin has been found to prevent these reactivity changes.

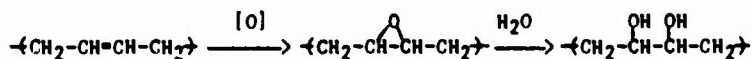
## INTRODUCTION

Poly bd R-45M resin, a hydroxyl terminated homopolymer of 1,3-butadiene, is widely utilized in the aerospace industry as a major component in the binder of solid propellant systems. This resin has many desirable properties, including low temperature flexibility, low viscosity, excellent stress and strain characteristics, high solids loading capability, low cost, and low signature of the finished rocket motor. However, the aging characteristics of the resin are such that its rate of reactivity with isocyanates in propellant formulations may increase during storage for prolonged periods at ambient temperatures. As a result, the pot lives of propellant mixtures prepared from the same lot of Poly bd R-45M resin may differ significantly over a period of months. This difference in reactivity can pose a problem for the formulator, who under certain circumstances may continually have to make alterations in the formulating process to compensate for the reactivity increase.

## DISCUSSION

Several hypotheses have been proposed to explain this aging process associated with Poly bd R-45M resin. All of these hypotheses involve either mechanisms which increase molecular weight and/or functionality or catalyze the urethane formation reaction. Increases in molecular weight/functionality might be caused by reaction of trace epoxide groups in the resin or by oxidative degradation of the resin. The presence of metals or acids would catalyze the reaction of Poly bd R-45M resin and isocyanates.

Since Poly bd R-45M resin is a homopolymer of 1,3-butadiene, each repeating unit contains a double bond. These points of unsaturation are susceptible to gradual oxidation either by peroxides or by atmospheric oxygen to form epoxides. These epoxides could potentially react with any water present to produce glycols (Scheme 1). Such an increase in functionality would result in increased crosslinking of the polymer and consequently in shorter pot life.



Scheme 1.

Another mechanism involving epoxides which would increase functionality and molecular weight is the intermolecular addition of a hydroxyl group to an epoxide (Scheme 2). However, experiments indicate that epoxide content remains constant upon aging Poly bd R-45M resin. Thus, a sample of the resin, having an initial gel time of 115 minutes and epoxide content of 0.053%, after aging for 4 months at 135°F gave a gel time of 69 minutes and an epoxide content of 0.057%. Storage of the resin under nitrogen also did not prevent reactivity increase (75 minutes) or affect epoxide content (0.055%). Therefore, it is unlikely that this mechanism is operant.



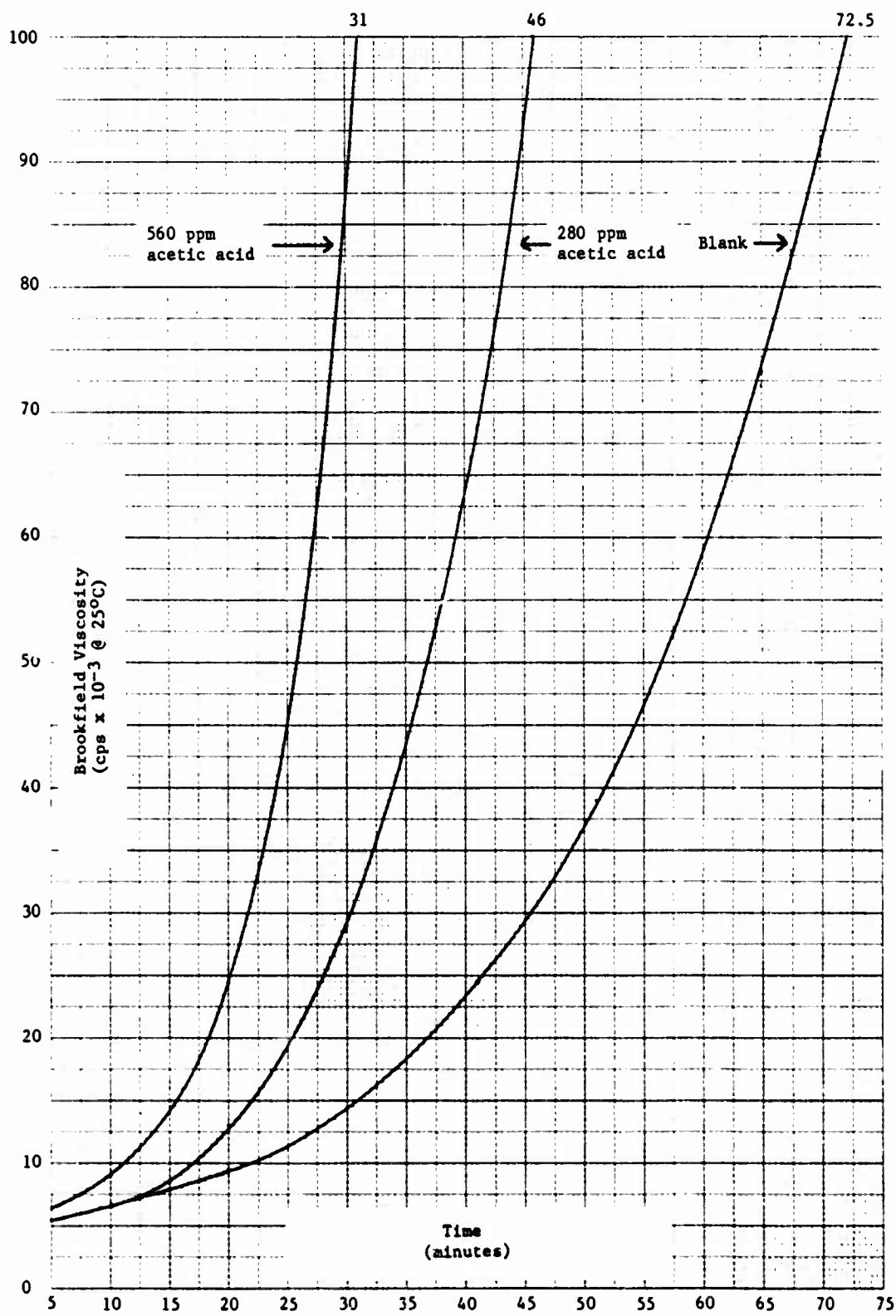


Figure 1.  
Effect of Added Acetic Acid on Gel Time

## RESULTS

Solutions of stabilizers in Poly bd R-45M resin were prepared and stored in an air-circulating oven at 135°F to accelerate the aging process. No attempt was made to exclude air from the samples, except as noted. All solutions contained 1% by weight of stabilizer.

A gel time test was devised to measure relative reactivity. The viscosity of a mixture of the Poly bd R-45M resin solution and Isonate 143L, a carbodiimide-modified diphenylmethane diisocyanate, at a 1.05 NCO/OH ratio is measured at 25°C. The time required for the reaction mixture to reach a viscosity of 100,000 cps is arbitrarily defined as the gel time and is a measure of the reactivity of the aged resin.

The results using a variety of stabilizer/Poly bd R-45M resin solutions are presented in Table I. The 2,2'-methylenebis-(4-methyl-6-*t*-butylphenol) (AO 2246) is the standard antioxidant added to inhibited grades of Poly bd R-45M resin. The AO 2246 was found to be ineffective in the prevention of reactivity change, although viscosity did remain constant. Initially, the rate of reactivity change was slowed by the AO 2246 when compared to the blank, but by the end of the aging period their gel times were comparable. The AO 2246 is a free radical scavenger<sup>7</sup> and traps the HO(R)OH formed from decomposition of active oxygen species, preventing crosslinking of the resin (Scheme 3; step C). Hence, no increase in viscosity occurs. However, the AO 2246 apparently prevents neither acid formation nor increased functionality arising from the decomposition of native active oxygen species.

Phenyl didecyl phosphite (PDP), while quickly reducing active oxygen levels to near zero, was totally ineffective at preventing reactivity change and viscosity increase. A combination of AO 2246 and PDP slowed the rate of reactivity change considerably when compared to PDP alone, but again large increases in viscosity occurred. This increase may be a result of the transesterification of the phosphite ester with the Poly bd R-45M resin, since the presence of AO 2246 did not prevent the increase in viscosity.

As mentioned previously, the addition of *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine initially resulted in a reactivity decrease, probably due to its basicity (Scheme 3; step B). Upon aging, only a small increase in reactivity occurred and no increase in viscosity was observed. The *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine evidently also acts to prevent the formation of new active oxygen species (Scheme 3; step A) in the Poly bd R-45M resin, eliminating for the most part an increase in functionality and crosslinking.

Triphenylphosphine (TPP) also initially results in a reactivity decrease. Furthermore, TPP totally prevents reactivity changes upon aging of TPP/Poly bd R-45M resin solutions. Like *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine, TPP partially restores the resin to its original reactivity by acting as an acid scavenger (Scheme 3; step B). According to the hybrid hypothesis, however, complete restoration of reactivity cannot be achieved, as irreversible functionality increase and crosslinking have already occurred (Scheme 3; step C). Only the reactivity increase caused by acid catalysis can be overcome once aging has occurred. TPP apparently also prevents formation of new active oxygen species, obviating the possibility of oxidative degradation and concomitant reactivity increase.

A further advantage of TPP is that, unlike *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine, it does not react with isocyanates and, therefore, is not incorporated into the polymer network. Thus, TPP may act as a stabilizer for the cured propellant system, preventing oxidation and subsequent degradation of physical properties.

Experiments were conducted to determine both the effective range of concentration of TPP and other phosphine equivalents of TPP. All triaryl phosphines tested were as effective as TPP in preventing reactivity increases of Poly bd R-45M resin aged at 135°F. Diaryl alkyl phosphines were somewhat less effective and aryl dialkyl and trialkyl phosphines were ineffective at preventing increases. A concentration of 0.5% appears to be the minimum amount of TPP required to effectively stabilize Poly bd R-45M resin.

## CONCLUSION

Triphenylphosphine has been identified as an effective stabilizer against reactivity increases observed with Poly bd R-45M resin upon prolonged storage at ambient temperatures. Other triaryl phosphines also appear to be effective stabilizers. These phosphines apparently act as acid scavengers and as antioxidants, preventing the formation of active oxygen species, whose decomposition over a period of time leads to increased reactivity of Poly bd R-45M resin with isocyanates.

135°F Aging Time (months)	Blank		2,2'-methylene- bis-(4-methyl-6- t-butyl phenol)		N-cyclohexyl- N'-phenyl-p- phenylenediamine		Blank		Phenyl didecyl phosphite		Phenyl didecyl phosphite + 2,2'- methylenebis- (4-methyl-6-t- butyl phenol)		Triphenyl- phosphine		Triphenyl- phosphine		N-cyclohexyl- N'-phenyl-p- phenylene- diamine			
	rel time (min)	viscosity (cps, 25°C)	rel time (min)	viscosity (cps, 25°C)	rel time (min)	viscosity (cps, 25°C)	rel time (min)	viscosity (cps, 25°C)	rel time (min)	viscosity (cps, 25°C)	rel time (min)	viscosity (cps, 25°C)	rel time (min)	viscosity (cps, 25°C)	rel time (min)	viscosity (cps, 25°C)	rel time (min)	viscosity (cps, 25°C)	rel time (min)	viscosity (cps, 25°C)
0	115	5496	119	6055	119	6134	81	6193	81	6193	81	6193	81	5996	81	5996	81	6134	81	6134
1	76	6193	91	6095	103	6134	68	-	75	7373	79	7373	89	5898	94	-	85	-	-	-
2	74	6289	82	5628	100	6628	55	6684	65	8257	71	8257	90	6095	95	5701	74	6134	74	6134
3	-	-	79	6387	93	6148	53	7008	47	9535	63	8945	90	6331	94	6016	83	6311	83	6311
4	49	6427	74	6128	83	6193	52	7373	42	8945	58	8945	90	6193	94	6045	82	6331	82	6331
5	-	-	-	-	-	-	48	7176	-	-	-	-	91	6291	93	5996	76	6291	76	6291

1. All samples were stored in an air-circulating oven at 135°F(57°C).

2. All solutions were prepared with 1% by weight antioxidant.

Table I.  
Poly bdp R-43M Resin Accelerated Aging Study

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