

## Addition Cure HCR: Impact of Inhibitors on the Elastomer Cure Profile

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**ABSTRACT:** This paper discusses the effect of inhibitor type, level and combinations of the inhibitors on the cure profile of addition cure silicone HCR (High Consistency Rubber). The purpose of the paper is to provide assistance to the formulator in selecting the type and level of cure inhibitor to achieve a specific cure profile.

Among the many advantages of the use of addition cure in HCR is the ability to create a compound with extremely rapid cure speed. Rapid cure speed it is desirable because it decreases the amount of time it takes to produce a component and increases the tool and capital equipment utilization. This increase in production directly impacts the profitability of the manufacturing operation. Addition cure compounds with up to six months shelf life are available commercially. This study is targeted at compounds intended for final mixing in or near the production environment. In these instances the mixed pot life can be measured in days and the overall cost of the compound can be significantly reduced. Addition cure compounds can be made very cost effective (Ref. 1) by using the appropriate combination of inhibitors and low levels of platinum catalyst. Mixing can be accomplished on relatively simple equipment such as a two roll mill. The select use of inhibitors can be used to adjust the cure profile to accommodate the specific equipment and component that the compound is intended for.

### Introduction

Three important areas have been the focus of this study;

1. The effect of inhibitor type and inhibitor level on workable pot life
  - o This impacts the ability to mix and produce parts
2. The impact of inhibitor on cure speed, and molding characteristics
  - o This directly impacts the cost to produce parts
3. The effect of inhibitor on final mechanical properties.
  - o The selection of inhibitor should not impact final mechanical properties

Using this criteria we report the results of the effectiveness of 3 different inhibitors. Tetramethyltravinylyclopentasiloxane (MVC) was determined to be a special category of inhibitor and its effects will be examined separately.

### Selection of inhibitors

The inhibitors were selected based on literature research, industry knowledge and FDA CFR 21 food contact regulations. In the FDA regulations, there are 5 allowable inhibitors for food contact in coatings,

Table 1: FDA allowed inhibitors, (Ref.2)

IUPAC Name	CAS #	Allowed, weight %
3,5-Dimethyl-1-hexyne-3-ol	107-54-0	0.53
1-Ethynylcyclohexene	931-49-7	0.64
Bis(methoxymethyl)ethyl maleate	102054-10-4	1.0
Methylvinylcyclotrisiloxane	68082-23-5	Any
Tetramethyltravinylyclopentasiloxane	2554-06-5	Any

Of these inhibitors, the bis(methoxymethyl)ethyl maleate is normally used for inhibition of liquid silicones in bath applications and not generally in HCR applications. Tetramethyltravinylyclopentasiloxane is a less volatile species than methylvinylcyclotrisiloxane and better suited to HCR applications.

In addition to the materials permitted by the FDA CFR21, a synergistic combination with a peroxide was included in the evaluation. Based on the information contained in patent number US 20110015336 2, (Ref. 3)-BUTANONE PEROXIDE, CAS 1338-23-4 was also added in the study.

Table 2: Selected inhibitors

ID code	IUPAC Name	Abbreviation	Source
M	Tetramethyltravinylyclopentasiloxane	MVC	Andisil® MVC
E	1-Ethynylcyclohexene	ETCH	Sigma-Aldrich
S	3,5-Dimethyl-1-hexyne-3-ol	Surfynol	Sigma-Aldrich
D	2-BUTANONE PEROXIDE	DDM	Sigma-Aldrich

Pot life was evaluated through a combination of instruments and observations. The basic plastic flow data was obtained through the use of a Plastometer, ASTM D 926 (Ref. 4). A Monsanto MDR 2000 rebuilt by MonTech with MonTech software was used to determine the Scorch time (Ts), the Time to 90 % cure, (T90), the minimum viscosity ML, and the Maximum torque, MH. ASTM D 5289, (Ref. 5). The cure temperature of the experiment was standardized at 350°F. The duration of the test was five minutes.

Each compound was allowed to age at room temperature of approximately 70°F with simply a plastic film dust cover to minimize contamination. Tests were repeated at approximately 24 hour intervals in both the Plastometer and the MDR.



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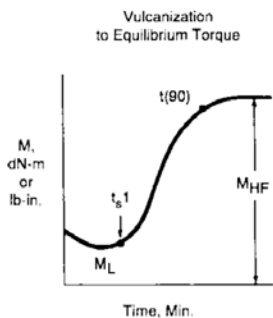


Fig. 1: Cure curve from ASTM D 5289 (Ref. 5).

### Determination of cure speed and flow characteristics

In accordance with ASTM D 5289 the onset of cure is taken as the time to scorch,  $T_s$ , while the time to cure was taken as  $T_{90}$ .

The value of  $M_H$  was used as a check to ensure that the material had cured properly while the value of  $M_L$  is used to indicate whether or not the compound had begun curing during the pot life determination.

Two levels of each of the four inhibitors were evaluated. Combinations of two different inhibitors were also tested. Part of the reason for this portion of the experiment was to determine if synergy exists between the different types of inhibitors. As is reported in the patent (Ref. 3), the use of the peroxide is claimed to have a synergistic effect on inhibitor performance. This synergy was not observed in these experiments.

### Inhibitor effect on Final mechanical properties

Selected formulations were tested according to ASTM D 412 (Ref. 6) to determine hardness, tensile strength and elongation. Using the data from the MDR, specifically, the maximum torque  $M_H$ , it was determined that the MVC inhibitor was interfering with the final mechanical properties of the experimental compound. One additional sample compound was made up which included a higher level of XL 10 cross-linker. This compound showed final torque values at  $T_{90}$  that were similar to the other compounds. From this it was suggested that the additional vinyl from the MVC was impacting the final mechanical properties of the compound. Compounds incorporating MVC will be addressed separately.

### Experimental Procedure

In addition to the selection of inhibitors previously noted in Table 2 the following materials were sourced from AB Specialty Silicones for the experiment;

- Andigum Base HS 3441, 40 durometer and,
- Andigum Base HS 3471, 70 durometer; fume silica base
- Andisil® XL 10, 7.55 mmol / gram 45 cSt methyl hydrogen /dimethyl copolymer;

- Two different hardness base's were selected, a 40 durometer, Andigum Base HS 3441 and a 70 durometer, Andigum Base HS 3471. A sufficient quantity of each base was compounded with the 0.75% Andisil® XL 10 cross-linker to act as a master batch for the remaining experiments.

These materials were used to prepare a large batch of compound for each durometer. Each large batch incorporated 0.75 weight % cross-linker which had previously been determined to be near an optimum level for mechanical properties in these bases.

In order to facilitate incorporation of the platinum on the laboratory two roll mill, a special blend was prepared consisting of; 0.5% Karstedt platinum catalyst in Andisil® VS 165,000 combined with 6% RS 812S fume silica from Evonik for viscosity control.

The platinum catalyst level was set at 5 PPM. This level was selected as the lowest level which could be precisely measured in our laboratory setting. A further reduction in catalyst level is entirely possible and could result in further significant cost savings in the formulation.

### Inhibitor masterbatch

Each of the inhibitors was prepared into a masterbatch with the HS 3441 base.

These master batches were used to incorporate the inhibitor into the compound. The high level and low level of inhibitor was tested in both 40 and 70 durometer compounds.

In using a two roll mill there were several challenges in incorporating an adequately high level of inhibitor. The target dispersion in the 40 durometer base was 10% however this proved to be very difficult using the two roll mill. For the Surfynol (ID "S"), MVC (ID "M") and DDM (ID "D") a concentration of 5% by weight was achieved on a two roll mill. After melting, the ETCH (ID "E") was incorporated at 7.35%.

The incorporation of ETCH provided some additional difficulties. ETCH is a solid at room temperature and required melting prior to incorporation. The ETCH was heated to 40° C and added to the 40 durometer base on a two roll mill which had been preconditioned to a temperature above ambient. An addition level of 7.35% was achieved. Fortunately ETCH does not begin to crystallize immediately upon reaching room temperature and remained liquid for some time after melting was accomplished. It's possible that with specialized equipment a higher level of concentration could be achieved, conversely the inhibitors may be purchased from a number of commercial sources pre-dispersed in a compatible silicone carrier.

For each of the inhibitors selected a separate master batch was made for each type. This was compounded into the Andigum base HS 3441 and was used in all subsequent experiments. The following table documents the formulation for each master batch.



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Table 3: Inhibitor concentration in compound, concentration designation, repeat for 40 and 70 durometer;

ID	High % Set 1	Low % Set 2
M	0.5	0.05
E	0.5	0.05
S	0.5	0.05
D	0.5	0.05

As noted previously, the MVC samples are not included in the results tables.

Each of the inhibitors was incorporated at 0.5% for a high level and 0.05% for low level.

One test batch was prepared for each inhibitor at two levels in both the 40 durometer and 70 durometer compound of base and cross-linker. A total of 16 batches was prepared. These batches were thoroughly mixed with 10 passes on a two roll mill prior to the addition of the platinum catalyst.

For the second stage of the experiment the inhibitors were combined into a blend of two different types

Table 4: Inhibitor combinations

ID Code	1 <sup>st</sup> inhibitor, weight%	2 <sup>nd</sup> inhibitor, weight %
DE2	0.05	0.05
DS2	0.05	0.05
ES2	0.05	0.05
DM2	0.05	0.05
MS2	0.05	0.05
ME2	0.05	0.05

The combination of inhibitors was only tested on the 70 durometer base. Also due to the confounding factor of the higher vinyl containing MVC (Sample ID “M”), combinations containing MVC were not subject the tensile testing.

Table 5. Mechanical property test results

	Duro-meter	Tensile, (lbf/in <sup>2</sup> )	Elongation %	Tear (lbf/in)
40-D1	37	1220	707	142
40-S1	33	1186	699	150
40-E1	36	1204	715	155
70-S1	62	921	418	129
70-E1	64	889	387	128
70-D1	66	1000	407	148
70-DS2	72	1050	291	135
70-DE2	NT	970	266	124
70-ES2	71	1000	279	128

These mechanical property results indicate that the selection of inhibitor had little effect on the final mechanical properties. For this experiment all master batches were prepared in Andigum Base HS 3441, a 40 durometer general-purpose fumed silica base. The HS 3441 base was also used to prepare the 40 durometer compounds. To understand the effect of hardness, Andigum Base HS 3471, a 70 durometer general-purpose fumed silica base was also used.

### Discussion of mechanical property results

Analytical analysis of vinyl concentration in a base is rather difficult. An optimum level of cross-linker was determined empirically by prior experimentation to be approximately 0.75 weight %. Since the level of cross-linker as a ratio to the vinyl concentration can range from 130% up to 300% of stoichiometric equivalence the 0.75 weight % level was deemed to be adequate.

The use of MVC (Sample ID “M”) as an inhibitor resulted in a significantly higher vinyl concentration than could be accommodated by the selected cross-linker level. This resulted in a lower-than-expected  $M_H$  value which was interpreted as an indication of under cure.

Additional experiments were then performed using a higher level of cross-linker. The resulting Rheometer data clearly indicated a much more complete cure and even suggested that MVC may be acting as an additional network cross-link site which could also modify mechanical properties. This work is beyond the scope of this paper but does present some intriguing possibilities for mechanical property modification in conjunction with the cure inhibition effect. The MVC introduced a new set of variables into the experiment and the mechanical property tests were not performed.

In order to hold as many variables constant as possible the level of hydride chosen was selected to be near the optimum for mechanical



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properties based on the previous empirical determination of the vinyl content of the base.

The use of MVC as an inhibitor contributes a significant amount of vinyl which changed the stoichiometry in the test batches. A second set of MDR samples was run with an increased level of hydride which illustrated the improved performance of the base when adequate hydride is available to consume all the available vinyl.

Table 6. MDR results comparison with increased cross-linker level. The maximum torque value is taken as an indication of the completeness of cure.

Property	As compounded	Increase crosslinker
M <sub>L</sub>	0.68	0.75
M <sub>H</sub>	7.16	16.62
T <sub>s</sub>	0.32	0.21
TC <sub>90</sub>	0.99	0.44
Plasticity	235	200

### Pot life/Working life evaluation

Pot life/Working life was qualitatively determined through examination of the fully catalyzed and mixed batch and its behavior on a two roll lab mill during preparation of specimens for the MDR.

Several factors were observed and integrated into an assessment of the end of working life. These included;

- The inability of the compound to band on the mill
- Cracking or roughness on the edge of the compound after passing through the two roll mill
- “Nervy” behavior, the uncured compound exhibiting elasticity when stressed

The selection of a test measurement method and an appropriate value for determination of mixed pot life/worklife is dependent upon the specific compound and the intended process.

Rheometer data can be used to establish a quantitative value for pot life. As the material begins to react at room temperature the scorch time, T<sub>s</sub>, becomes shorter to the point where it can no longer be injected into the mold. Similarly, M<sub>L</sub> increases or ceases to be a minimum and instead the torque value rises continuously from the closing of the platens. At some point the initial viscosity becomes too high for it to fully flow into the mold or through the extrusion die.

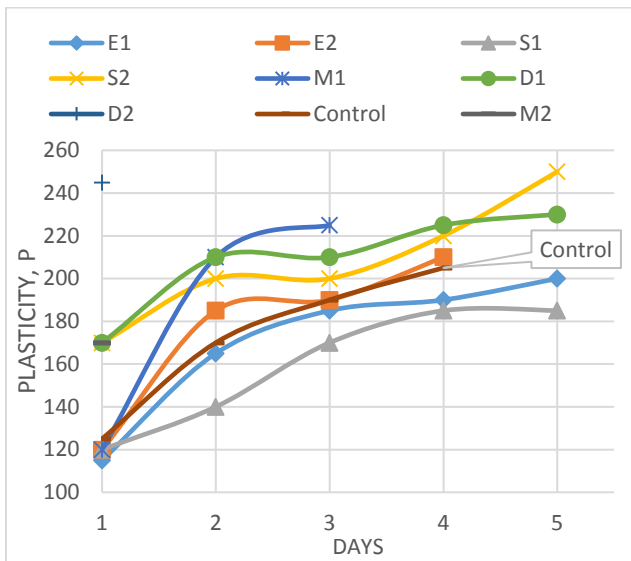


Fig. 2: 40 Duro Plasticity

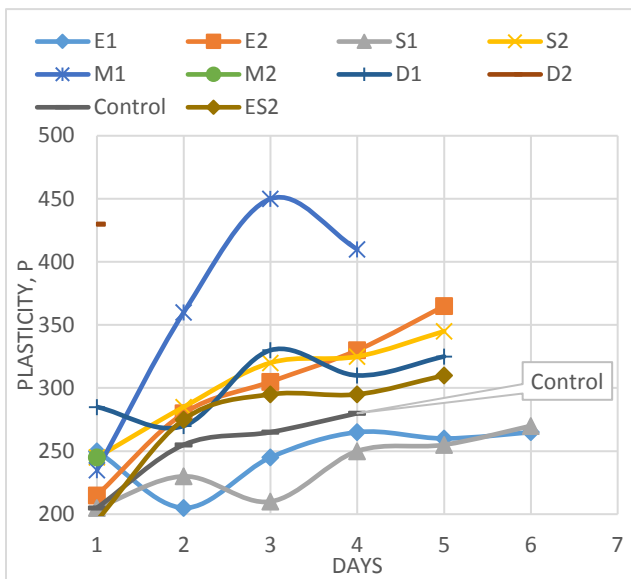


Fig. 3: 70 Duro, Plasticity

Data from the Plastometer indicated a drift upward in the values over time. The control sample had all ingredients except inhibitor and Pt catalyst. All of the other samples listed included inhibitor and catalyst. Samples D2 and M2 exhibited rapid viscosity increases and could only be measured at a single data point.

Assuming no cross linking reaction was taking place, the increasing plasticity reading should be attributed to structuring of the compound after the shearing and incorporation of the crosslinker.



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### Rheometer data

The following six graphs summarize the results of the evaluation of the inhibitors which provided adequate mixed pot life.

In addition to the three inhibitors by themselves in the 70 durometer compound three combinations of two inhibitors were combined at their lowest level and evaluated for pot life stability. These combinations are noted in Table 4

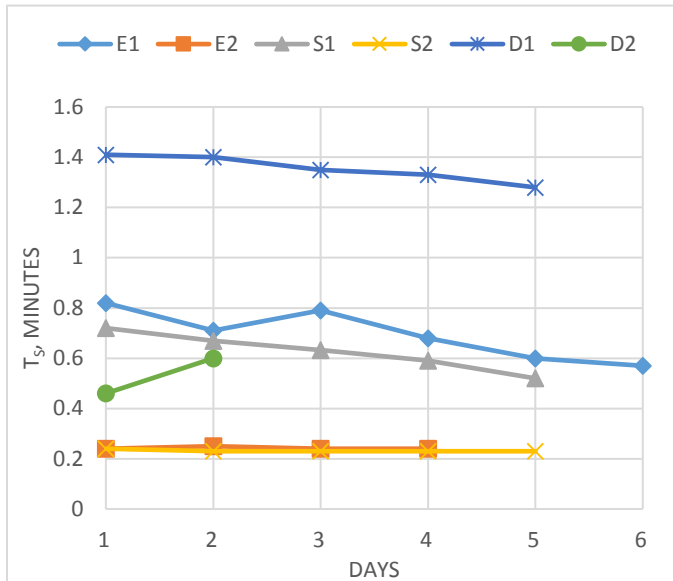


Fig 4: 40 Duro T<sub>g</sub>

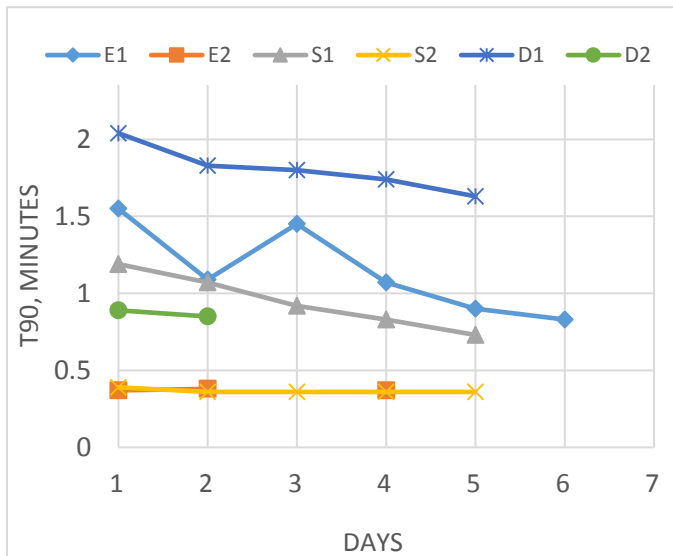


Fig. 5: 40 Duro, T<sub>90</sub>

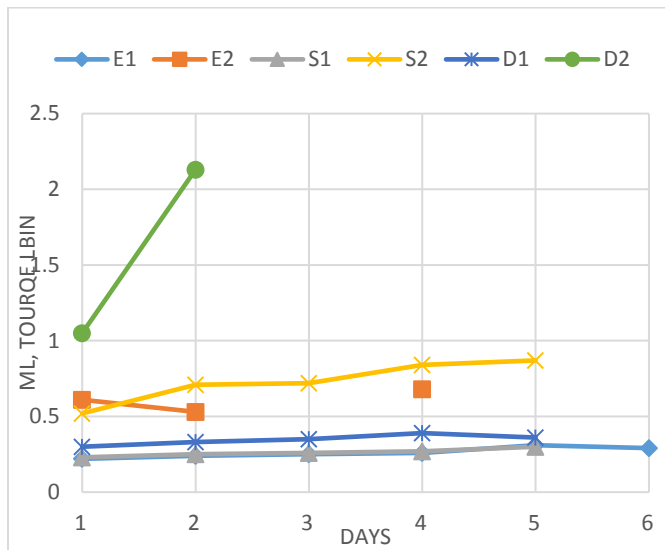


Fig. 6: 40 Duro ML

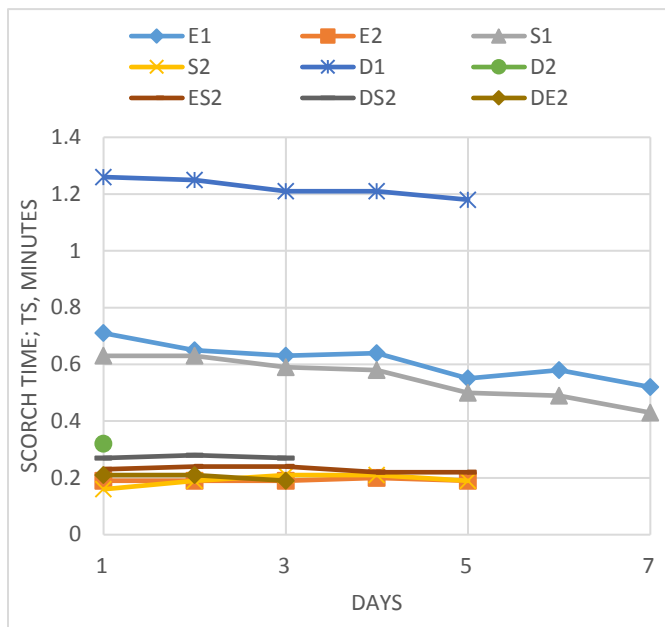


Fig. 7: 70 Duro, T<sub>s</sub>



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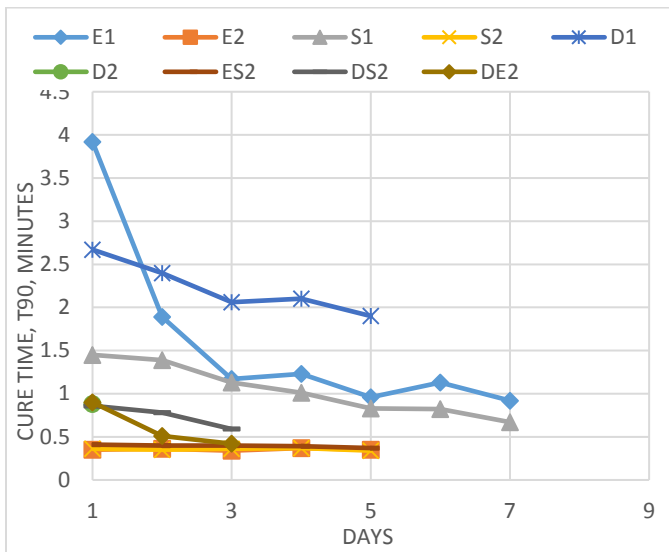


Fig. 8: 70 Duro, T<sub>90</sub>

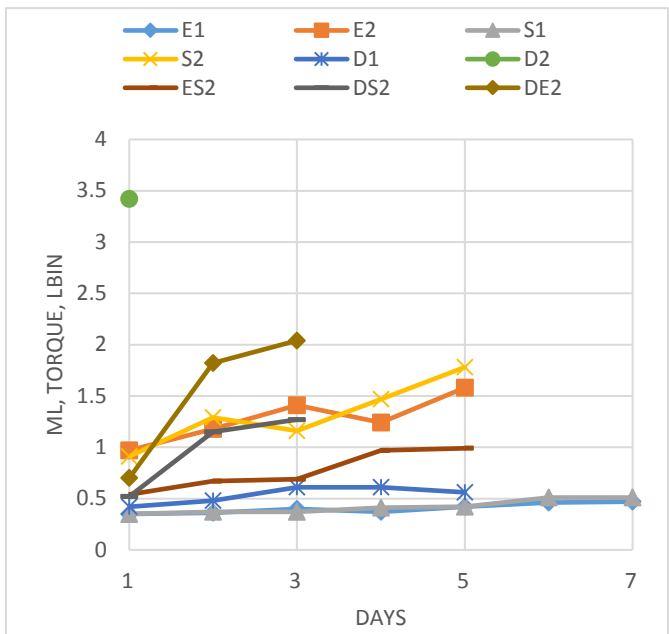


Fig. 9: 70 Duro, M<sub>l</sub>

### Detail examination of TS and T<sub>90</sub>

The next two graphs look at the impact of three different inhibitors in the impact of varying the inhibitor level on scorch time, T<sub>s</sub> and cure, T<sub>90</sub>. Each inhibitor type is represented by a different marker symbol and the scorch value, T<sub>s</sub> is represented with a dotted line. By selecting a desired scorch time on the dotted line and dropping down to the inhibitor level weight %, a starting point concentration of inhibitor can be estimated. Moving vertically on the time axis at that concentration will intersect the cure time line, T<sub>90</sub>, providing an

estimate of the amount of time for the reaction to proceed to 90% of completion.

These data points were generated by taking the average T<sub>s</sub> and T<sub>90</sub> for the compounds which exhibited three days or more of pot life.

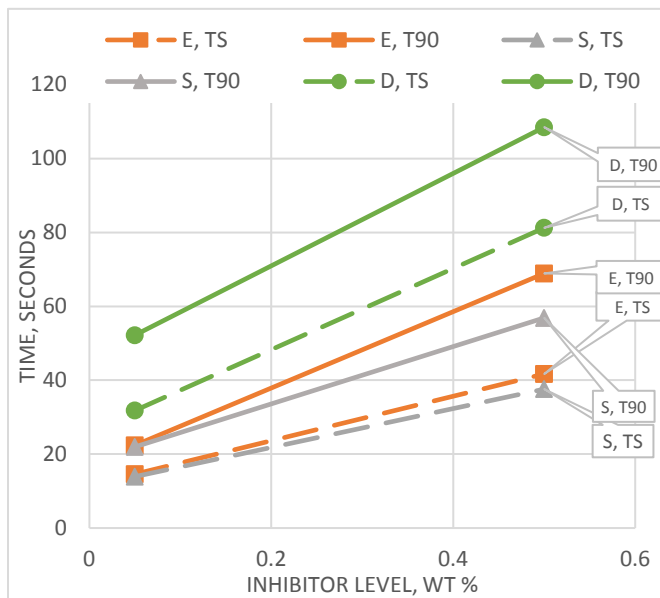


Fig. 10: 40 Duro, T<sub>s</sub> & T<sub>90</sub> vs Inhibitor

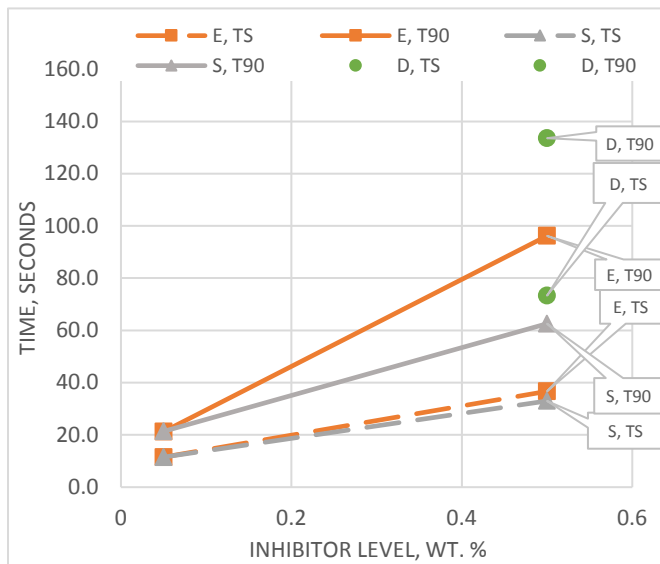


Fig. 11: 70 Duro T<sub>s</sub> and T<sub>90</sub> vs Inhibitor

For the 70 durometer base, the peroxide inhibitor, (“D”), by itself did not provide adequate pot life at the low level to obtain valid data, thus rendering interpolation problematic.



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### Discussion of results:

These results demonstrate the relative ease of formulating single component room temperature stable HCR addition cure compounds.

The ability to utilize the addition cure system in HCR confers many advantages for the fabricator. HCR compounds can utilize existing tooling and avoid the use of expensive injection molding machines while still retaining the benefits of FDA approval. Addition cure systems offer finished products with no requirement for postcure to remove residual material such as peroxide decomposition products.

Processing times of addition cure systems can be much faster than peroxide cure and this provides a significant increase in the capital utilization of equipment and tooling. Because of the very rapid transition from scorch to final cure, addition cure compounds can provide significant cost savings when considered from the overall manufacturing process. The component size does play a role in determining whether the use of addition cure is cost competitive.

It may be possible to reduce the platinum level even further than 5 PPM for additional cost savings. Unlike peroxide, platinum acts as a true catalyst in the system. The mechanical properties are better controlled by modifying the cross-linkers and other vinyl containing modifiers (Ref. 7).

While a minimum scorch time, TS, must be determined for each particular application, it is clear that with the appropriate selection of inhibitors an adequate safety margin can be achieved between mixing, initiation of the fabrication process and the onset of cure. For ease of compounding it is recommended that master batches of each component be prepared in advance. It is also entirely feasible to obtain a complete compound in two components which can then be mixed on site and delivered to the molding or extrusion operation. One week or more mixed pot life can be achieved with little impact on mechanical properties while still retaining the desired rapid cure speed and very low consumption of platinum catalyst.

Consideration should be given to the selection of fillers and pigments potentially used in the compound due to the well-known possibility for interaction between the platinum catalyst and such materials as sulfur, amines and other catalyst poisons.

Synergistic effects between the peroxide (Sample ID "D") and other inhibitors were not observed as claimed in Ref. 3 under these experimental conditions.

Further work could explore the relationship between MVC (sample ID M) as an inhibitor and its effect on final mechanical properties.

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#### Notes

The authors declare no competing financial interests.

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