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MECHANICAL STABILIZATION OF RIGID PVC COMPOSITIONS

Thomas C. Pedersen
Rheogistics LLC
Picayune, MS USA

Robert R. Kwapisz
Rheogistics LLC
Picayune, MS USA

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ABSTRACT

This paper presents rheological data on simple rigid PVC compositions lubricated paraffin wax, calcium stearate, and oxidized polyethylene wax. These three materials comprise the most widely used lubricant system for rigid PVC in North America. The influence of certain paraffin wax characteristics will be discussed. Rheological data will be presented on simple PVC pipe formulations containing only lubricants, calcium carbonate, and pigment together with diminishing amounts of heat stabilizer, including one compound without any heat stabilizer. These compositions all display remarkable rheological stability, and demonstrate that lubricants are, in fact, mechanical stabilizers. The North American paraffin wax based lubricant system is an excellent starting point for rigid PVC formulations containing new stabilization technology. The challenge in working with stabilizer free rigid PVC compositions is managing early color development and pinking.

INTRODUCTION

For more than 40 years, rigid PVC pipe formulations in North America have been lubricated with combinations of paraffin wax, calcium stearate, and oxidized polyethylene wax. The range and limits of ingredient used in North America’s PVC pipe formulations for pressure applications is published by the Plastic Pipe Institute in their technical report TR-2[1]. The composition is essentially as follows:

Ingredient	Usage Level
PVC Resin	100 parts
Tin Stabilizer	0.30 – 1.00 phr
Paraffin Wax	0.60 – 1.50 phr
Oxidized Polyethylene Wax	0.00 – 0.30 phr
Calcium Stearate	0.40 – 1.50 phr
Titanium Dioxide	0.50 – 3.00 phr
Calcium Carbonate	0.00 – 5.00 phr
Process Aid	0.00 – 2.00 phr

The paraffin waxes used are typically refined from crude oil or produced synthetically from ethylene or methane. The waxes are predominately straight chain alkanes. The chemical formula of the ideal paraffin wax for rigid PVC is:

$$C_{32}H_{66}$$

The range of carbon numbers present typically varies from C-26 to C-40. Paraffin wax delays fusion and reduces melt temperature. All paraffin waxes also contain branched or non-normal molecules.

Calcium stearate is a salt of C-16 to C-18 fatty acids derived from triglycerides, typically tallow or palm oil. The chemical formula of calcium stearate is:

$$Ca\text{-}(C_{18}H_{35}O_2)_2$$

Calcium stearate increases the viscosity of the lubricant system and is often considered a fusion promoter in rigid PVC pipe formulations.

The third component is oxidized polyethylene wax, which is derived from ethylene. These materials are complex higher molecular weight molecules with a chemical formula of:

$$C_{100+}H_{200+}O_{?}$$

Every oxidized polyethylene wax is different, and their impact on rigid PVC rheology is very complex. In general oxidized polyethylene wax helps to moderate melt temperatures and improve metal release.

Lower carbon number paraffin waxes (C-28 and below) increase the speed of PVC fusion, become soluble in rigid PVC, and tend to soften the melt. Higher carbon number paraffin waxes (C-40 and above) strongly delay the speed of PVC fusion, remain insoluble in rigid PVC, and stiffen the melt. The ideal paraffin lubricant for rigid PVC is somewhere in between (about C-32). The effect of different size paraffin molecules on Brabender fusion time, torque, and melt temperature has been observed to be as follows:

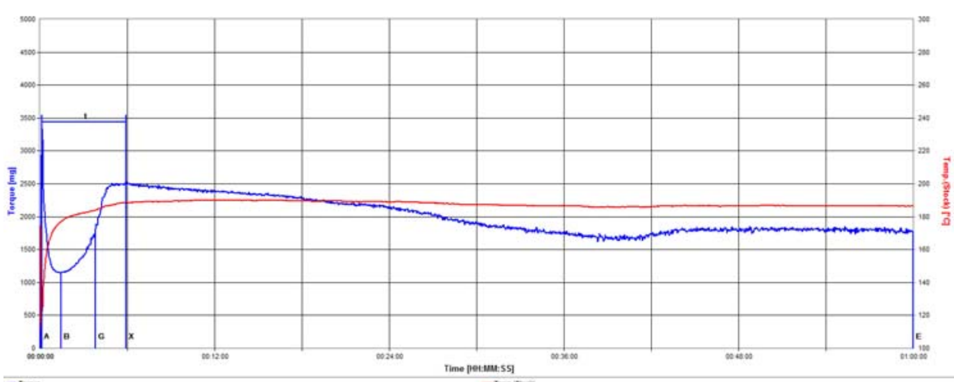
Carbon Number	Fusion Time	Fusion Torque	Equil. Temp
26	166 sec	21.3 Nm	>195°C.
32	352 sec	15.2 Nm	188°C.
40	2,120 sec	10.1 Nm	188°C.
100+ (PE Wax)	182 sec	18.9 Nm	>195°C.

Fusion time increases and fusion torque decreases as the carbon number of a paraffin wax increases. The use of a polyethylene wax (non-oxidized) in place of paraffin wax results in faster fusion and higher fusion torques. The polyethylene wax tends to be incompatible with rigid PVC and, in some cases, exudes from the melt.

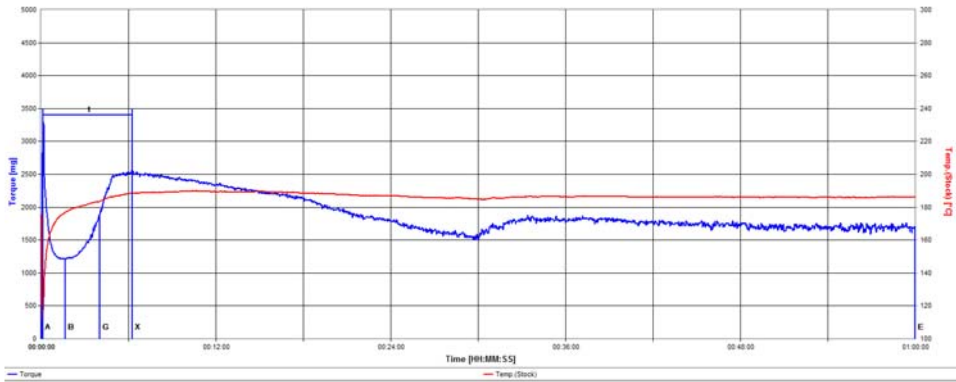
EXPERIMENTAL

Brabender torque rheometry test results for a PVC pipe formulation lubricated with 1.30 phr of paraffin wax, 0.20 phr of oxidized polyethylene wax, and 0.65 phr of calcium stearate, 5.00 phr of calcium carbonate, 1.00 phr titanium dioxide and different levels of a non-lubricating 19% methyl tin heat stabilizer are as follows:

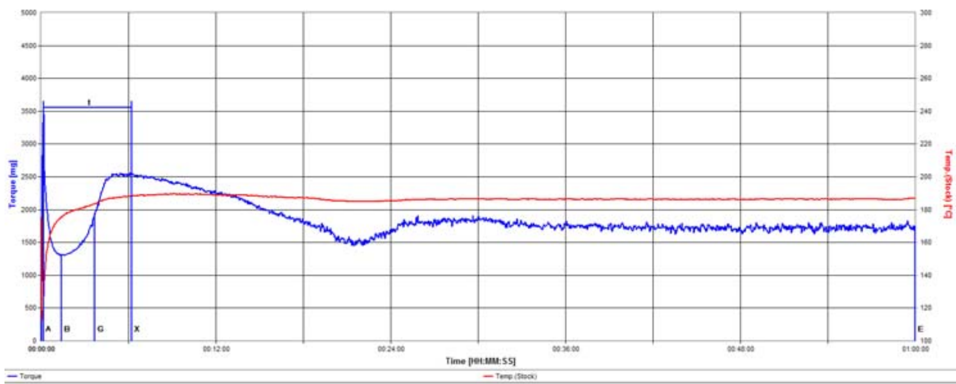
1. 0.50 phr Tin Stabilizer



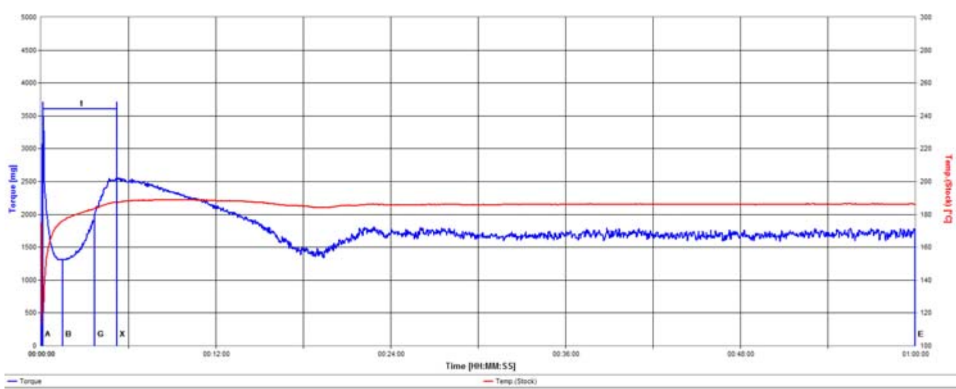
2. 0.25 phr Tin Stabilizer



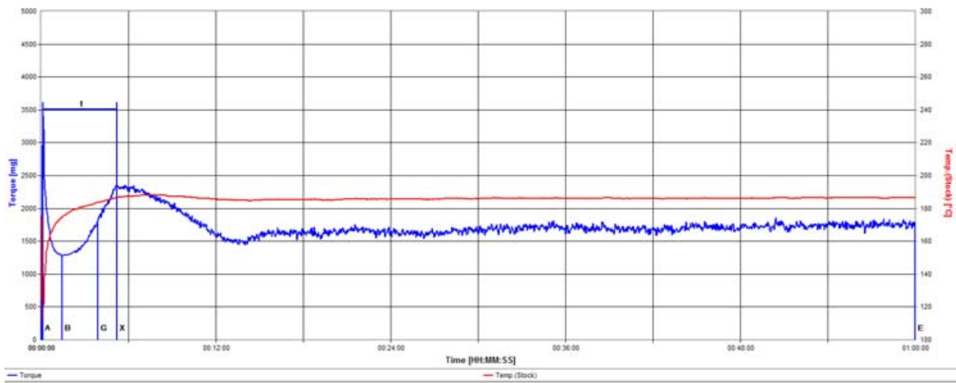
3. 0.125 phr Tin Stabilizer



4. 0.0625 phr Tin Stabilizer



5. Stabilizer free



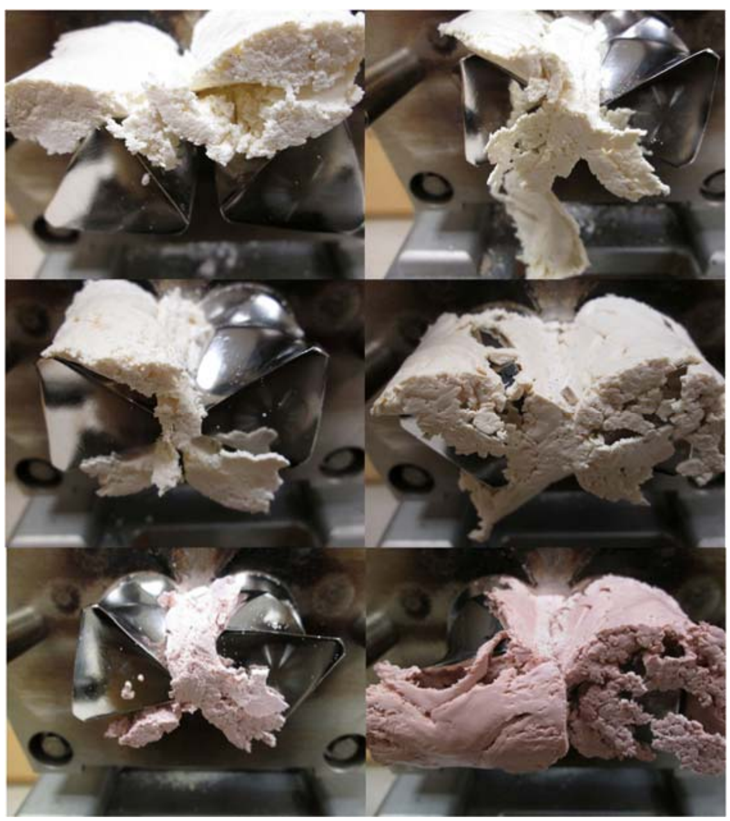
DISCUSSION

As the level of stabilizer is reduced, minimum compaction torque increase slightly; fusion torque stays about the same and is perhaps slightly lower for the stabilizer free compound. Fusion time is about the same for the five different stabilizer levels as is melt temperature and ending melt torque. The post fusion shape of the curve is different. There is a long transition as between fusion torque and final melt torque in the formulation containing 0.50 phr of tin stabilizer. This length of this transition is shortened with each reduction in stabilizer content. The ending melt torques and melt temperatures remain about the same for the five different stabilizer levels. The overall rheology of the compound free of heat stabilizer remains remarkably stable during the hour long test.

Tin stabilizer became the material of choice in North America years ago because the PVC pipe industry favored bright white pipe. Today, a variety of pipe colors are produced in North America including white, blue, green, brown, yellow, gray, and others.

The following chart demonstrates color development for the five different stabilizer levels after one hour of processing (top row), 10 minutes of processing (middle row), and 5 minutes of processing (bottom row).

When all the tin stabilizer is removed, the compound becomes pink after 5 minutes or 10 minutes of processing. After an hour of processing, it becomes grayish brown. After one hour of processing, the ending color is comparable the compounds containing heat stabilizer. Another view of the 5 and 10 minute results for compounds containing 0.1250 phr (top), 0.0625 phr (middle) and no stabilizer (bottom) follows:



Early pinking is virtually eliminated by the presence of only 0.0625 phr of 19% tin stabilizer. We have been unable to find any other material that has a similar impact on pinking at such a low usage level.

CONCLUSIONS

The paraffin wax, calcium stearate, and oxidized polyethylene wax lubricant system long popular in North America provides rheologically stable rigid PVC compounds with or without heat stabilizer. Combinations of paraffin wax, calcium stearate, and oxidized polyethylene wax act as mechanical stabilizers, and provide a strong foundation on which to develop new metal free stabilizer systems. Tin stabilizer is currently the most efficient chemical available today to manage color development of rigid PVC compositions. Some rigid PVC applications, where color is not a major concern, may be able to eliminate the use of heat stabilizer thru careful formulation of the lubricant system.

REFERENCES

1. TR-2, PPI PVC Range Compositions, List of Qualified Ingredients, 19 March 2013, Plastics Pipe Institute, Irving, TX 75062 USA