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B. F Goodrich Chemical Company

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DEVELOPMENT CENTER

Staff Technical Report No. 126

THE EVOLUTION OF (DIBUTYLTINDICHLORIDE AND HCl) FROM RIGID PVC COMPOUNDS STABILIZED WITH DIBUTYLTIN BIS(OCTYL THIOGLYCOLATE)

By

L.B. Crider
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Closure Report for Project 2894-266-1

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OBJECTIVE

The long range objective of this work is to improve the thermal stability and reduce the porosity of extruded pipe made from rigid PVC compounds stabilized with dibutyltinthioglycolate (S-8). Our immediate objective is to develop a method for measuring the relative rates at which dibutyltindichloride and HCl are volatilized at elevated temperatures and to determine whether a relationship exists between porosity and dibutyltindichloride volatilization. The development of a sensitive and reproducible method for measuring the rates at which these components are volatilized would also provide a useful tool for studing the synergistic effects of other compounding ingredients in PVC compounds stabilized with organotin thioglycolates.

SUMMARY AND CONCLUSIONS

The use of dibutyltin bis (octyl thioglycolate) as a processing stabilizer in PVC serves two functions. It acts as a chlorine scavenger and it also apparently does some patching of the sites of unsaturation in the polymer back bone created by dechlorination. Chlorine split off by thermal decomposition reacts with the stabilizer to yield dibutytindichloride (DBTDC) plus an octyl thioglycolate radical.

The dibutyltindichloride is evolved from the PVC compound as a volatile product which can be readily measured by mass spectrometry. The failure to observe octylthioglycolate as a volatile product is strong evidence that this radical must become attached to the polymer backbone.

At elevated temperatures (450°F.) the initial evolution of HCl as a volatile product is coincident with a sharp decline in the evolution of DBTDC. This event apparently signals the depletion of the effective stabilizer in the compound.

The evolution of DBTDC from a typical rigid PVC compound is detectable after 15 seconds of exposure at 450°F. The rate of volatilization is sharply increased at about 5 minutes and reaches a maximum at about 6 1/2 minutes. A sharp decrease in the rate for DBTDC is always accompanied by a sharp increase in the rate for HCl.

Increasing the amount of stabilizer in the sample increases the time at which the maximum for DBTDC occurs. A similar effect can be noted by increasing the amount of calcium stearate in the compound.

The results of this study did not yield any conclusive evidence that HCl or DBTDC evolution is responsible for porosity in extruded pipe.

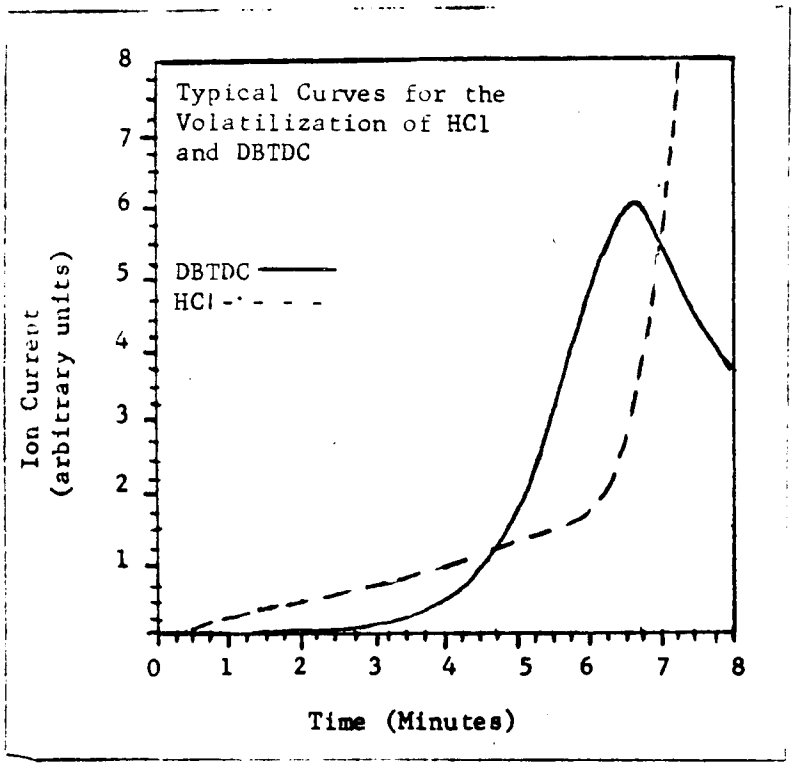


Figure A

It is suggested that calcium stearate may have a deleterious effect on both stability and porosity. It acts as an HCl scanvenger but not as a polymer stabilizer since the acid radical produced by HCl attack does not attach itself to the polymer backbone but is volatilized as stearic acid.

Typical rates of volatilization for DBTDC and HCl from a PVC pipe compound (Geon 8750) are shown in the figure at the left.

FUTURE WORK

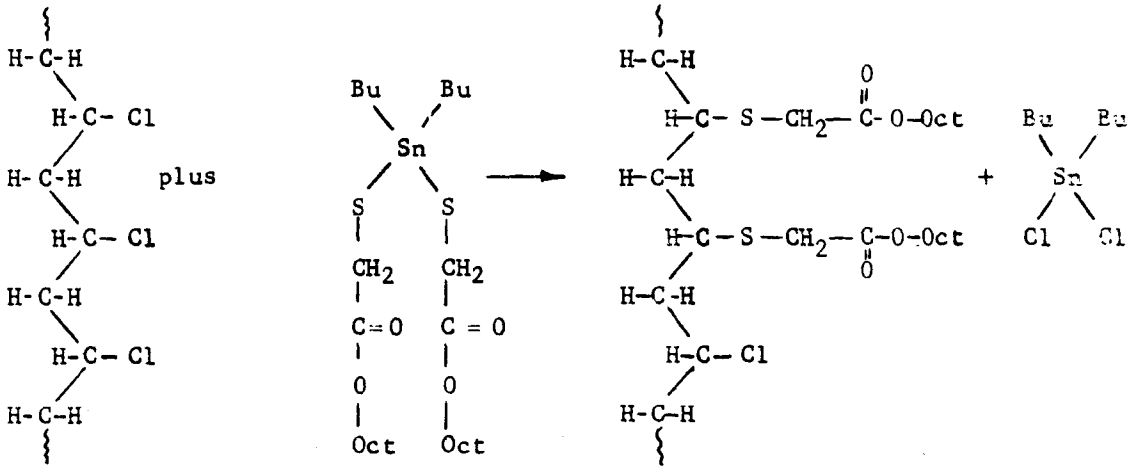
Further exploitation of this method for studying the synergestic effects of other compounding ingredients in rigid PVC is now in progress. Our initial efforts will be concentrated on further measurements of rates for HCl and DBTDC volatilization as a function of stabilizer concentration. These measurements will be made in the absence of lubricants. Similar rates will also be measured for other organotin stabilizers of the type [Bu_2 Sn Y_2] but containing different Y groups. These same tests will then be repeated with the addition of lubricants. These data, combined with experimental extrusion results will hopefully reveal some of the interplay that must occur between the polymer, stabilizer and lubricant at extrusion temperatures.

INTRODUCTION

The recent introduction of a new concept in screw design for extruders used in the processing of rigid PVC cubes has greatly increased the rate at which pipe compounds can be extruded. At these higher rates the stock temperatures may be in excess of 450°F. With our standard pipe compounds, such a Geon 8750 and 8759, our customers have experienced difficulties in obtaining quality pipe and phenomena such as porosity and chicken tracking have forced them to lower output rates.

The problem of porosity was rationalized as being related to the formation of volatile materials in the stock during the exposure to these higher temperatures in the extruder. At the beginning of this investigation our limited objective was to identify the materials that were being volatilized. Much to our surprise we learned that the initial evolution of volatiles was very low in HCl and high in dibutlytindichloride. The emphasis in our work on this problem was then shifted to measuring the relative rates at which HCl and dibutyltindichloride are volatilized with the hope that these results would reflect the cause of porosity.

The dibutyltindichloride is formed in rigid PVC compounds from the reaction of chlorine with the dibutyltin bis (octyl thioglycolate) stabilizer. The failure to observe octyl thioglycolate as a volatile product from this reaction strongly supports the proposition that this radical must become attached to the polymer chain at the site vacated by the chlorine:



The work of Frye, Horst and Paliobagis[1][2][3] on the chemistry of organotin stabilizers (using radioactive tracer techniques) has done much to illucidate the role that these compounds play in the stabilization of PVC.

A set of experiments was designed to show whether PVC is butylated by organotin stabilizers of the type [Bu_2 Sn Y_2] under conditions normally used to study the thermal degradation of the polymer. Using ^{14}C tags in the Cl position of the butyl groups it was shown[1] that it is unlikely that any butylation of the polymer occurs. Tagging the Y groups with ^{14}C suggested[3] that the stabilizing action of the organotin compounds arises from reactions wherein the polymers chlorine atoms are exchanged for the stabilizers Y groups. ^{113}Sn tagged compounds showed that most of the Sn is lost due to degradative reactions. The retention of a small amount of radioactivity was rationalized as being due to the existance of a coordinative linkage formed between the stabilizer's Sn atom and the donor atom (Cl) present in the polymer's molecular structure.

With this background, it appeared that the ability to measure the relative rates at which dibutytindichloride and HCl are volatilized would give us some further insight on the effects of adding more (or less) stabilizer and of varying the amount and types of lubricants used in a rigid PVC compound. An attempt could be made to correlate these rate curves with porosity. The difficulties in doing this were apparent before we started, however. First of all, the volatilization rate is conditioned by two important factors i.e., the rate at which the volatile molecules are formed and the rate at which they are diffused out of the compound cube or particle. Reproducible results would then be dependant on using cubes that have exactly the same physical dimensions. Cube-to-cube variations in composition (inhomogeneity) presents another problem. In spite of these limitations, the results obtained from our initial measurement of rates of volatilization for HCl and dibutyltindichloride show that the method is sensitive to stabilizer concentration and other differences in rigid compound formulation.

DISCUSSION AND RESULTS

The procedure used to study the volatilization of dibutyltindichloride and HCl in rigid PVC cubes is our standard mass spectrometer method for the analysis of volatiles in polymers. Since this procedure is quite well known I shall only describe it briefly in this report.

The sample is contained in a small glass bottle (0.5 dram). Since the cubes from production material are not uniform in size, some effort was made to select cubes that were 1/8" square. Eight cubes of this size are placed in the sample container which is then inserted into the vacuum chamber that has been preheated to 450°F. The temperature is measured on the walls of the chamber and is not a measurement of the stock temperature. One minute is allowed to evacuate the chamber and to pre-heat the sample. The valve between the sample chamber and the ion source is then opened and a mass spectrum is scanned every 15 seconds.

Separate sample runs are required for the measurement of the volatilization rates for HCl and dibutyltindichloride. Both components cannot be monitored from a single scan at 15 second intervals because of the gross difference in molecular weights. The ions that are monitored for HCl and dibutyltindichloride are monocomponent so that direct plots can be made of ion current vs. heating time. The identification of the ions is unequivocal since these are based on the natural abundance of the $^{37}Cl/^{35}Cl$ ratio for HCl and on the combined $Sn-Cl_2$ isotopes for dibutyltindichloride. (Calculating the relative abundance of the ions containing both tin and chlorine turned out to be a bit of a task because of the muliplicity of the Sn isotopes. This required writing a computer program to give us the relative abundance of ions containing SnCl $SnCl_2$, $SnCl_3$ and $SnCl_4$.)

Plotting the amount of ion current for each component at 15 second intervals gives a relative measurement of the rate of volatilization. To make this result quantitative would require a complete analyses of the total spectrum and a heat loss measurement at each 15 second interval. This amount of effort did not seem warranted since a relative rate can describe what is occuring in the sample cube.

A comparison of relative rates of volatilization for HCl and dibutyltindichloride (DBTDC) from samples of Vyram 3000, Geon 8750 and Geon 8759 are shown in Figure 1, 2 and 3.

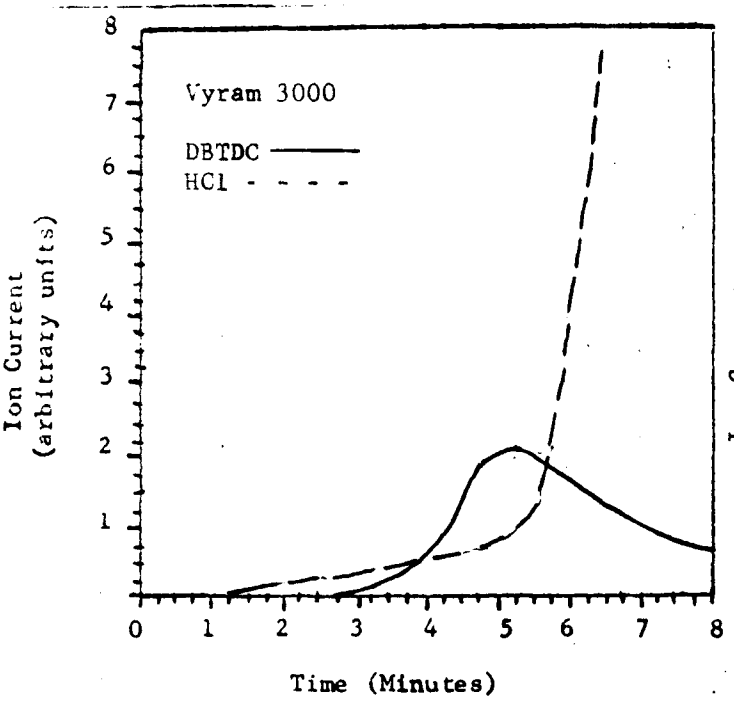


Figure 1

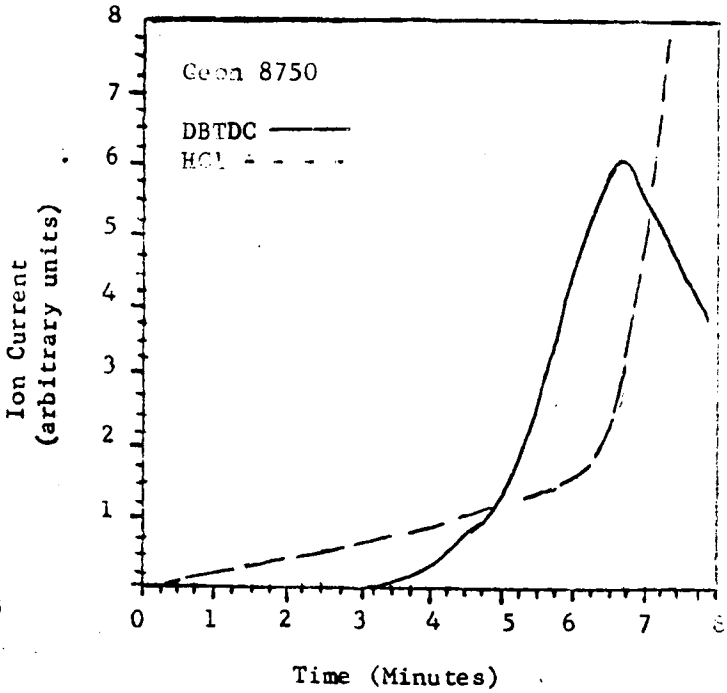


Figure 2

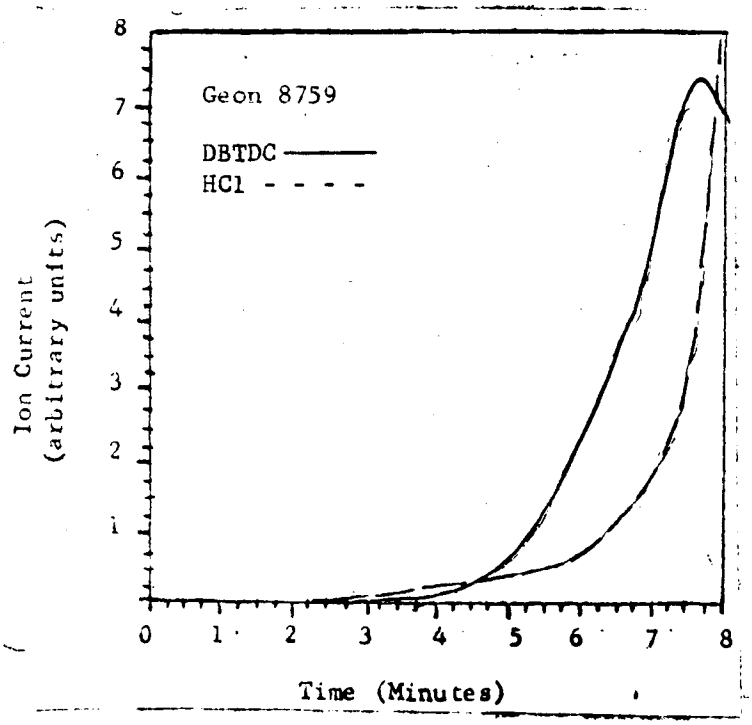


Figure 3

In all three cases, the evolution of HCl is retarded until the maximum for DBTDC is reached. This suggests that this event is coincident with the depletion of the effective stabilizer in the sample. The intensity of the maximum also reflects the concentration of tin stabilizer in the original sample.

X-ray fluorescence analyses[4] for Sn in Vyram 3000 and Geon 8759 are shown in Appendix I [run by Crobaugh Laboratories in Cleveland] The maxima for DBTDC in these samples reflects the higher Sn content of the Geon 8759:

	Sn Wt.%	DBTDC Max.
Vyram 3000	0.18	2950
Geon 8759	0.38	7000

[The reproducibility of the results for Sn obtained by X-ray fluorescence is remarkable and suggests that this instrument could be used to study the rate of volatilization of DBTDC on a quantitative basis]

The reproducibility of the rate curves for HCl and DBTDC are shown in Figure 4 and 5.

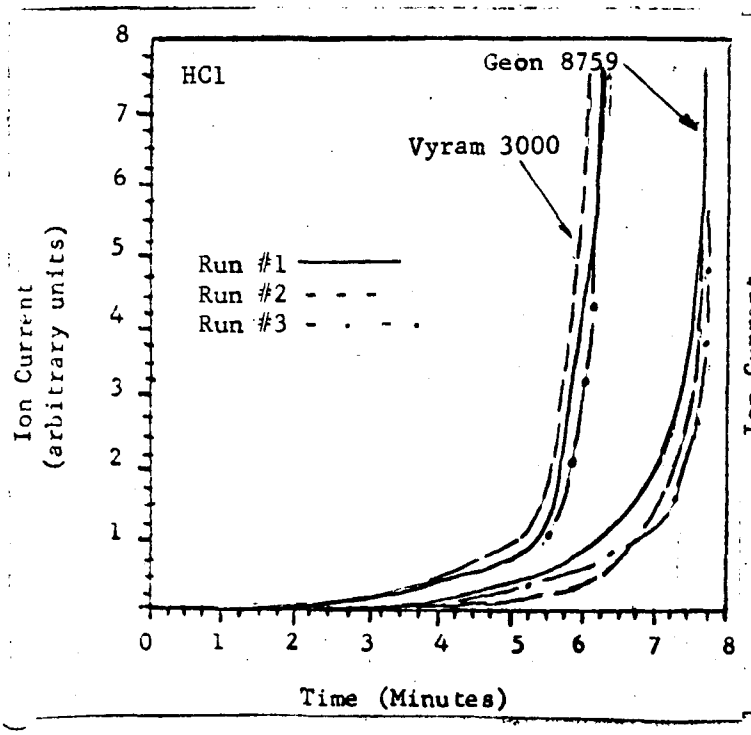


Figure 4

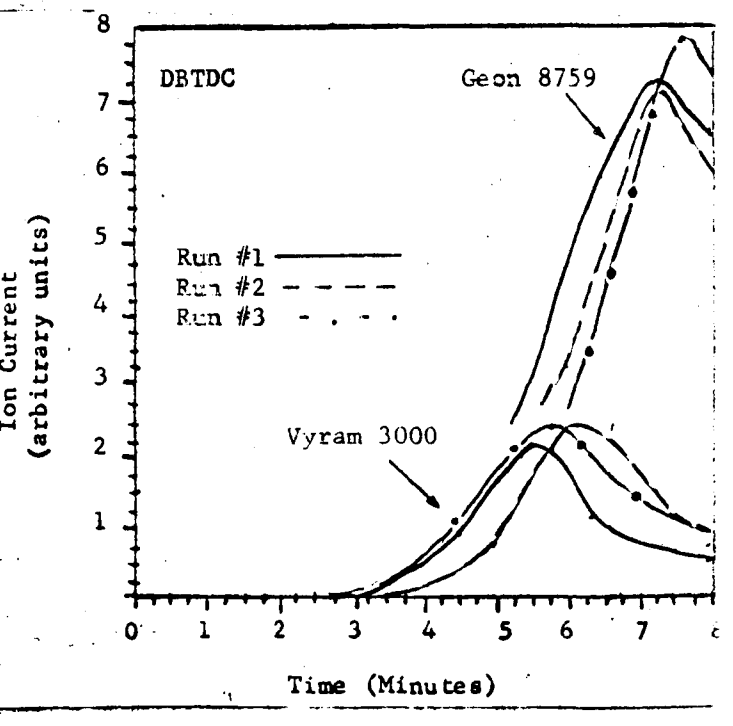


Figure 5

Although there are some differences in the curves obtained from three runs the overall reproducibility is good enough to reflect the gross difference in composition between Vyram 3000 and Geon 8759. The difference between Geon 8750 and Geon 8759 would not be as clearly defined.

The heat loss values measured at the end of the eight minute exposure at 450°F are as follows:

	Vyram 3000 Wt.%	Geon 8750 Wt.%	Geon 8759 Wt.%
Run #1	3.29	5.50	4.97
Run #2	3.40	4.93	4.74
Run #3	3.23	5.06	4.79

The lower heat loss value for Vyram 3000 is, in part, reflected by the lower tin stabilizer content. Part of the heat loss materials are also due to the volatilization of processing aids and other compounding ingredients. It now becomes of interest to determine whether the presence of these other compounding ingredients has an influence on the relative rate curves for HCl and DBTDC through some synergistic effects.

Our efforts to measure the effects of calcium stearate (1.3) on the relative volatilization rates for HCl and DBTDC gave results that were not reproducible. It is believed that this lack of reproducibility is related to lack of homogeneity in the test slabs. A comparison of the rates from duplicate runs are shown in Figures 6 and 7 for samples of Vyram 3000 (control) and from samples of Vyram 3000 containing an additional 1 part and 2 parts of calcium stearate.

Although the results are not reproducible, they do show that the addition of calcium stearate retards the evolution of DBTDC and HCl. The results from run #2 show that each additional part of calcium stearate added advances the maximum for DBTDC at least a full minute and that a corresponding effect is also evident for HCl.

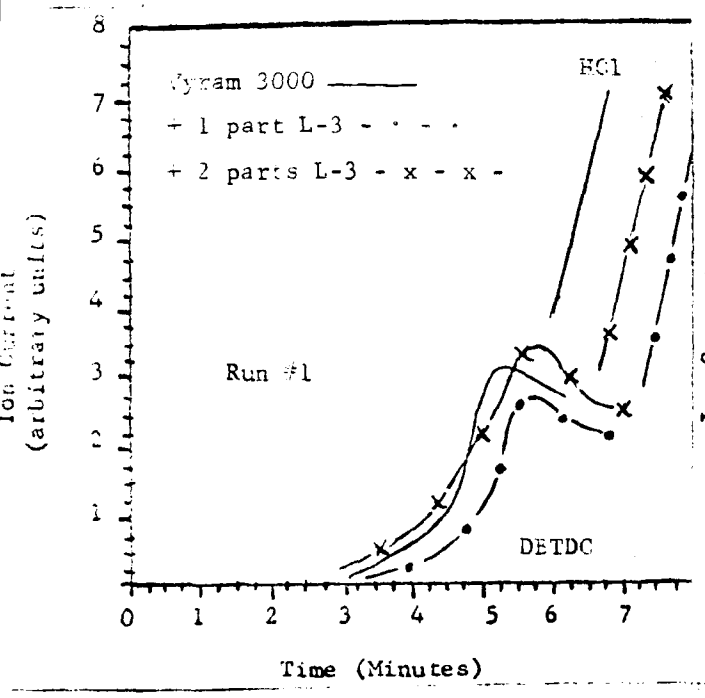


Figure 6

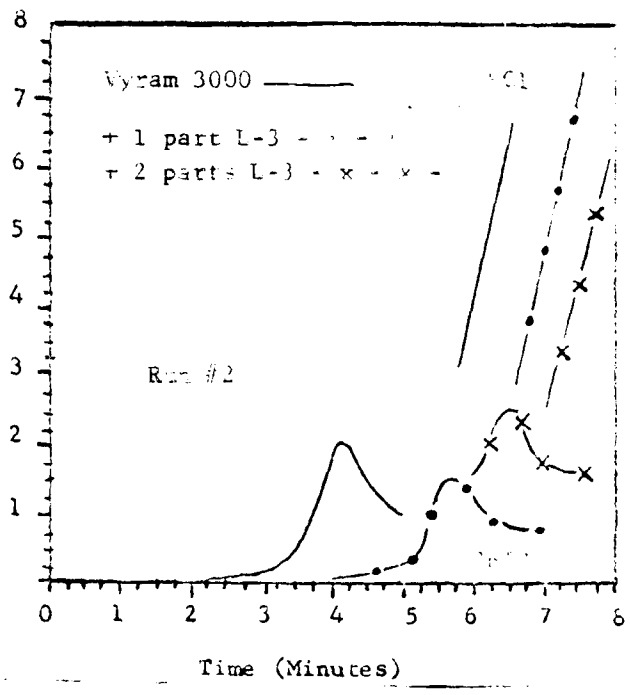


Figure 7

This data would support the theory that calcium stearate has some stabilizing effect and would act to conserve the tin stabilizer. The results from Run #1 would be difficult to interpret other than to suggest that there was poor mixing of the L-3 with the Vyram in preparing the samples on the mill.

The suggested stabilizing effect of calcium stearate at milling temperatures may also have some adverse effects as related to porosity. The evolution of stearic acid as a volatile product is most evident in PVC compounds containing calcium stearate.

The reaction of chlorine or HCl with calcium stearate is unlike that with the tin stabilizer in that the acid radical that is split off does not patch the vacant site in the polymer backbone but is expelled as a volatile product. It's value as a stabilizer is limited to the single function of acting as a chlorine scavenger. One can visualize this as having a deleterious effect since the damage to the polymer backbone is not repaired as would have occured if the chlorine had reacted with the tin stabilizer. This school of thought is a good arguement for the proponents that calcium stearate can create problems of porosity and poor stability at the temperature encountered at high extrusion rates.

A comparison of the relative rate curves for Vyram 3000 and Vyram 3000 plus 1 part of N,N' ethylene bis stearamide (L-9) shows an effect similar to calcium stearate. This data is shown in figure 8. The addition of 1 part of L-9 retards the evolution of both HCl and DBTDC about 45 seconds.

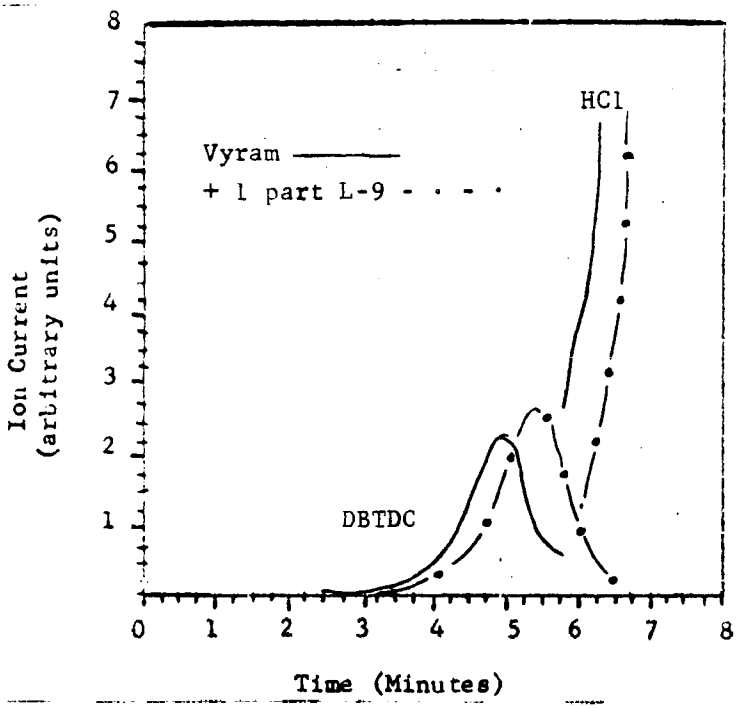


Figure 8

In summary, the results of this initial effort to use mass spectrometry to study the volatilization rates for HCl and DBTDC has furnished much confirming evidence about the chemistry of dibutyltin bis(octylthioglycolate) as a stabilizer in PVC. We strongly support the findings of Frye, et.al., that the Y groups become attached to the polymer backbone and that the dibutyltin is evolved as the dichloride. There is no evidence to support the claim of Kenyon[5] that stabilization of PVC by tin compounds of the type [Bu_2 Sn Y_2] must be due to the ability of the stabilizer to donate a butyl group to a polymer radical. If this were true, one would expect that the volatile materials would contain some [Cl_2-Sn-Y_2] or [BuCl-Sn-Y_2] and none can be found. The mass spectra is also absent of Bu-Sn-Cl_3 and $SnCl_4$.

The demonstrated ability of the method to reflect the addition of lubricants in PVC compounds certainly warrants our continued exploratation of this technique in studying the synergestic effects of other.compounding ingredients with organic tin stabilizers.

ACKNOWLEDGMENTS

The authors wish to acknowledge the contributions of John Nikora for recording and tabulating the mass spectral data and to J.R. Smith for writing the computer program to calculate the relative abundance of ions containing tin and chlorine.

BIBLIOGRAPHY

1. Frye, Alfred H., Horst, Raymond W., and Paliobagis, Marko A., "The Chemistry of Poly (vinyl chloride) Stabilization. III. Organotin Stabilizers Having Radioactively Tagged Alkyl Groups", J. of polymer Science, Part A., Vol. 2, p 1765-1784 (1964)

2. Frye, Alfred H., Horst, Raymond W., and Paliobagis Mark A., "The Chemistry of Poly (vinyl chloride) Stabilization. IV. Organotin Stabilizers Having Radioactively Tagged Tin Atoms." J. of Polymer Science, Part A, Vol. 2, p 1785-1799 (1964)

3. Frye, Alfred H., Horst, Raymond W., and Paliobagis, Marko A., "The Chemistry of Poly (vinyl chloride) Stabilization V. Organotin Stabilizers Having Radioactively Tagged Tin Groups." J. of Polymer Science, Part A, Vol. 2, p 1801-1814 (1964)

4. Laboratory Report R-7621, Crobaugh Laboratories, Cleveland, Ohio, April 6 1966 (attached as Appendix I)

5. Kenyon, A.S., Natl. Bur. Standards (U.S.) Circ No 525 91 (1953)

Laboratory Report

CROBAUGH LABORATORIES

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To: B. F. Goodrich Chemical Company
Development Center
Moore & Walker Roads
Avon Lake, Ohio 44012

Reporting Date April 6, 1966
No. R 7621
Date Received March 21, 1966
Material PVC Discs
Marked Please see below
P.O. No. 136 AL-33-2

[Note: These identifications were not known to Crobaugh Laboratories]

REPORT

	Sample No.	% Tin in P.V.C.
Geon 8759 1.5 pt. TM-180	71-1	0.23
Geon 8759 2.5 pt. CC-11	71-2	0.47
Geon 8759 2.5 pt. T-31	71-3	0.38
Vyram 3000	71-4	0.18
Vyram 3000	71-5	0.18
Geon 8759 2.5 pt. T-31	71-6	0.38
Geon 8759 2.5 pt. CC-11	71-7	0.48
Geon 8759 1.5 pt. TM-180	71-8	0.23
Geon 8759 2.5 pt. TM-180	71-9	0.45
Geon 8759 2.5 pt. T-31	71-10	0.38
Vyram 3000	71-11	0.18
Geon 8759 2.5 pt. TM-180	71-12	0.45

Respectfully submitted,

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Alex Sitkin

Alex Sitkin

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