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B. F. Goodrich Chemical Company
A DIVISION OF THE B. F. GOODRICH COMPANY
DEVELOPMENT CENTER

Degradation and Combustion Products From Poly(vinyl Chloride)

VI - Pyrolysis of Chlorinated PVC

by
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MAJOR OBJECTIVES

The major objectives of this research problem are:

1. to correlate the pyrolysis products from typical polymers with flammability, toxicity, corrosion and polymer structure, and

2. to develop the necessary technology for degrading polymers in the presence of air and for measuring the various degradation products.

LIMITED OBJECTIVES

The limited objectives of the current study were:

1. to determine the degradation products from two differently processed chlorinated PVC samples (aqueous chlorination vs. solvent swollen chlorination),

2. to determine the presence of any structural differences in the two samples as evidenced by high and/or low temperature pyrolysis and/or other analytical techniques, and

3. to predict, from the degradation products in an inert atmosphere, any possible toxic degradation products that would be evolved in an oxygen rich atmosphere.

SUMMARY AND CONCLUSIONS

1. Low temperature pyrolysis (300°C, in vacuum) of T-574 (Hi-Temp, Solvent swell chlorination) and of T-575 (Hi-Temp, aqueous chlorination) revealed differences due only to the medium of chlorination in which the two samples were prepared. The following summarizes these findings:

Sample	Degradation (300°C) Products	
T-574	HCl (major)	
	Benzene	
	Chlorobenzene	
	Dichlorobenzene	
	CCl_4	residual solvent
	$CHCl_3$	residual solvent
T-575	HCl (major)	
	Benzene	
	Chlorobenzene	
	Dichlorobenzene	

2. High temperature pyrolysis (600°C) revealed the following degradation profiles:

Product	T-574 ← Wt.% →	T-575
HCl	60.5	68.6
Volatile Hydrocarbon Fraction	13.1	5.7
Carbonaceous Ash	26.4	25.7

The volatile hydrocarbon fractions had the following compositions:

Product	T-574 ← G.C. Area % →	T-575
$CHCl_3$	2.3	nil
Benzene	46.6 (major)	25.8
CCl_4	46.6 (minor)	nil
Toluene	5.1	trace
C_2Cl_4	5.2	nil
Chlorobenzene	27.1	37.0
Dichlorobenzene isomeric	9.4	26.1
Dichlorobenzene	4.3	11.1

The higher level of HCl in the pryolyzate of T-575 indicates that a higher degree of chlorination had taken place in the preparation of this resin. This hypothesis is substantiated by the chlorine analysis (T-574 = 67.73*%, T-575 = 69.49%) and by N.M.R. analysis (see below) of the two polymers.

3. Nuclear magnetic resonance spectroscopy (J. Westfahl) indicated the following distribution of ~CHCl - CHCl-CHCl and ~ CH_2 - CHCl linkages (minor contributions from vinylidene linkages were not considered) in the two polymers:

	~ CH_2-CHCl ~ ← Mol. % →	~ CHCl-CHCl-CHCl~
T-574	53	47
T-575	4	96

4. The two chlorinated resins were submitted to R. Krueger at the Research Center for stability evaluations. The results of that study showed that when both resins were heated at 220°C, T-574 exhibited a 5.5 minute induction period (before dehydrochlorination began) while T-575 had a corresponding 8.5 min. induction period. The longer induction period of T-575 can be accounted for by the higher degree of chlorination (more ~CHCl-CHCl-CHCl ~ linkages) in this resin.

*due, in part, to residual solvent

5. Based on a knowledge of the degradation products in an inert atmosphere, the following combustion products would most probably result from the burning of T-574 and T-575 in air:

Resin	Probable Combustion Products
T-575	HCl, CO_2 and CO
T-574	HCl, CO_2, CO, unknown levels of phosgene

The phosgene in the combustion gases of T-574 would result from the pyrolysis of residual solvent and not from resin degradation. The amount of phosgene would be proportional to the residual solvent and this may be as high as 1.2 - 1.3%.