

B.F.GOODRICH CHEMICAL COMPANY
AVON LAKE DEVELOPMENT CENTER

Staff Technical Report No. 63

RESIDUAL MONOMERS & LOW TEMPERATURE
DEGRADATION PRODUCTS FROM GEON 351
& GEON 352 LATICES

by

L. B. Crider

Date Completed: June 25, 1964

Date Issued:

(LBC-31-64)

Distribution:

Avon Lake

R. J. Wolf
C. H. Lufter
N. G. Duke
Technical Council
G. L. Wheelock
E. J. Leeson
Geo. Antlfinger
Geo. Gateff
R. Kreager
J. W. Ryan
E. G. DeCapita
E. A. Collins
L. Chandler
CTF
File (2)

Brecksville

J. J. Shipman
L. Jimenez

Cleveland

R. D. Scott - A. Vittone
C. H. Alexander
D. Kent

Louisville

S. S. Michels
R. R. Taylor

3243

20563001

BFG03967

SUMMARY & CONCLUSIONS

The previous identification of 0.5 wt. % methyl chloride in a freeze coagulated sample of Geon 350X11 raised some questions as to the origin of the methyl chloride and the effects of this material on the measurement of residual vinyl chloride monomer in Geon 351 and Geon 352 latex.

The results from our current study shows that chloromethane and chloroethane are decomposition products from Geon 351 (VCl-methylacrylate copolymer) and Geon 352 (VCl-ethylacrylate copolymer) respectively. In both cases the decomposition begins at about 125 degrees C. and is quite pronounced at 150 degrees C. A degradation mechanism has been proposed based on a combined mass spectrometer-infrared study.

The mass spectrometer method for the analysis of vinyl chloride monomer in Geon latices gives results that are about 2X those obtained by the standard stripping method. Samples of stripped latex from Louisville storage were tested by both methods and gave the following results:

	Stripped Geon 351		Stripped Geon 352	
	M. S. Method	Standard Method	M.S. Method	Standard Method
	Wt. %	Wt. %	Wt. %	Wt. %
Vinyl Chloride	0.99	0.45	0.60	0.25
Methyl Chloride	0.04		--	
Ethyl Chloride	--		0.01	

The differences between the two methods have not been resolved but are believed to be due to the use of high vacuum and heat to extract the monomer in the mass spectrometer method while the standard procedure used steam stripping of the latex and a subsequent collection of the monomer fraction in a cold trap.

INTRODUCTION

It has been previously reported (1) that the two low temperature transitions which were observed in a differential thermal analysis of Geon 350X11 (VCl-methylacrylate copolymer) were due to the presence of methyl chloride in the latex. A mass spectrometer analysis obtained from a freeze coagulated sample of this same latex showed 0.5% methyl chloride. It was suggested that the unexpected presence of this quantity of methyl chloride in the dried latex must be due to decomposition of the polymer which could occur through the elimination of HCl and a subsequent attack of the ester group. The purpose of the current investigation was to determine the source of the methyl chloride and to measure the amount in a typical lot of production material.

- (1) Crider, L. B., "Volatiles in Geon 350X11" Memo Report to E. J. Leeson, Dec. 12, 1963 (LBC-54-63)

BFG03968

20563002

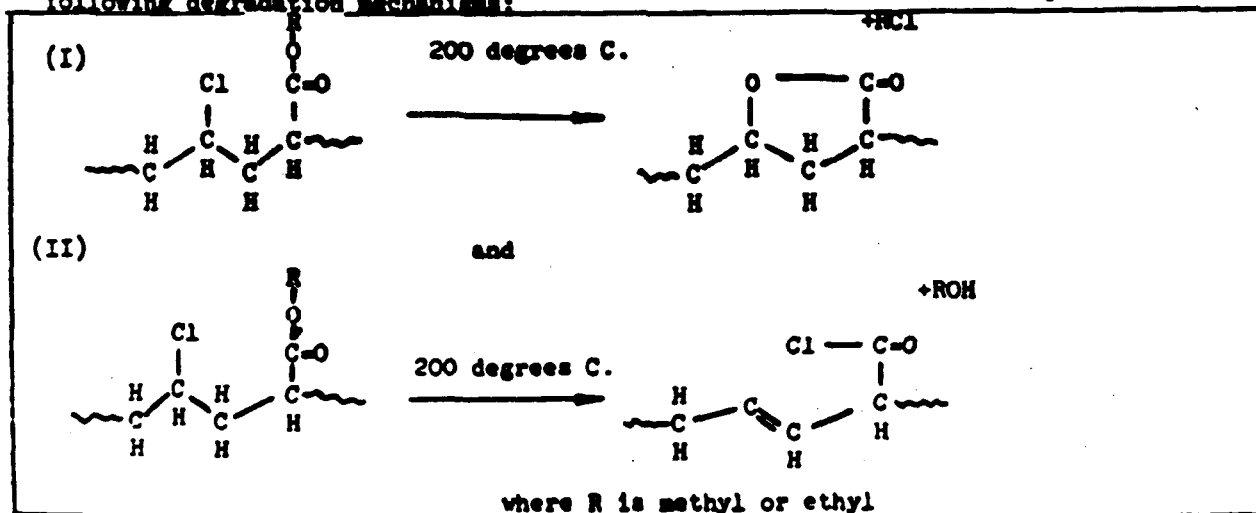
DISCUSSION & RESULTS

A further study of the volatile products in Louisville Geon 351 & Geon 352 confirms that methyl chloride and ethyl chloride are degradation products from VCl-methylacrylate and VCl-ethylacrylate copolymers respectively. Mass spectra were obtained from samples of freeze coagulated latex at temperatures of 100 degrees C., 125 degrees C., 150 degrees C. and 200 degrees C. The results of this study shows that trace amounts (100 ppm.) of methyl chloride and ethyl chloride are evolved on heating the latices at 125 degrees C. in vacuum for 5 minutes. At 150 degrees C. the decomposition rates are increased to yield 0.40 methyl chloride and 1.50% ethyl chloride in 5 minutes and at 200 degrees C. these same yields are increased to 6.76% and 3.19% respectively.

A summary of the results obtained from this study is given in Appendix I and Appendix II. It should be noted that the degradation products from the 351 latex (App. I) also includes, in addition to methyl chloride, appreciable amounts of methanol and aromatic hydrocarbons. The decomposition of 352 latex yields, in addition to ethyl chloride, sizeable amounts of ethanol and acetaldehyde along with smaller quantities of acrylic acid and aromatic hydrocarbons.

A degradation mechanism for both latices was developed based on the evolution of methyl chloride and methanol from Geon 351 and ethyl chloride and ethanol from Geon 352. The proposed decomposition route is elucidated by a comparison of the infrared spectra obtained from both latices before and after heat treatment at 150 degrees C. and 200 degrees C. (The I.R. work was done by J. W. Ryan). The heat treatment of both polymers resulted in oxidation which was shown in an absorption at 1770 cm^{-1} (5.65 μ). This absorption could result from the presence of an acid chloride, organic carbonate or a five membered lactone. The sample examined at 150 degrees C. showed only a very weak absorption at 1770 cm^{-1} and a correspondingly pale color. The 200 degrees C. samples were very dark in color and had very strong absorptions at 1770 cm^{-1} . None of the samples had absorptions characteristic of water, alcohol or free acid.

The combined mass spectrometer and infrared data tends to support the following degradation mechanisms:



20563003

BFG03969

The IR absorption at 1770 cm^{-1} may be attributed to the C=O in both structures I and II. The carbon-carbon double bond in structure II is evidenced by an absorption at 1640 cm^{-1} .

With this background, the mass spectrometer procedure for the analysis of residual monomers in latex samples of this type was modified to use a sample inlet temperature of 100 degrees C. to avoid any possible decomposition of the polymer. The undiluted latex sample is charged to the instrument through a rubber septum using a micro-syringe.

Analyses were made for both the stripped and unstripped latex samples received from Louisville (L-3793, 5/22/64). These results are given in Appendix I and Appendix II. It should be noted that the values obtained by the mass spectrometer method for residual vinyl chloride monomer in the latex are about 2X those obtained by the standard testing procedure (Procedure No. 387):

<u>Geon 351 Latex</u>			
	Stripped Wt. %	Stripped Wt. %	Unstripped Wt. %
	By M. S.	Proc. No. 387	By M. S.
VC1	0.99	0.45	1.13
<u>Geon 352 Latex</u>			
VC1 Monomer	0.60	0.25	1.72

The results obtained from the unstripped 351 latex also shows an appreciable amount of methyl chloride which at this temperature (100 degrees C.) could not be present due to decomposition. By contrast, the unstripped 352 latex shows only a trace amount (0.01%) of ethyl chloride. The results from the unstripped 351 latex suggest that some methyl chloride may be formed during polymerization.

20563004

BFG03970

Volatiles from Geon 351 Latex
(Louisville 5/22/64)

Geon 351 Latex @100 degrees C.

	Stripped Wt. %	Unstripped Wt. %
H ₂ O	54.61	53.36
Methyl Chloride	0.04	1.14
Vinyl Chloride	0.99	1.13
Heat Loss	55.64	55.63

Volatiles from Samples of Freeze Coagulated 351 Latex

Stripped Latex

	@100 degrees C. Wt. %	@100 degrees C. Wt. %	@150 degrees C. Wt. %	@200 degrees C. Wt. %
H ₂ O				0.86
Methyl Chloride	0.0062	0.0068	0.40	6.76
Vinyl Chloride	nil	nil	.0045	trace
Methanol	nil	nil	trace	0.27
Aromatics	nil	nil	trace	0.15
				8.04

Unstripped Latex

	@100 degrees C. Wt. %	@125 degrees C. Wt. %	@150 degrees C. Wt. %
Methyl Chloride	0.0064	0.0129	0.50
Vinyl Chloride	0.0007	0.0024	0.0048
Methanol			Trace
Aromatics			Trace

APPENDIX I

20563005

BFG03971

Volatiles from Geon 352 Latex
(Louisville 5/22/64)

Geon 352 Latex @100 degrees C.

	<u>Stripped</u> <u>Wt. %</u>	<u>Unstripped</u> <u>Wt. %</u>
H ₂ O	45.15	44.53
Ethyl Chloride	0.01	0.01
Vinyl Chloride	0.60	1.72
Heat Loss	45.75	46.26

Volatiles from Samples of Freeze Coagulated 352 Latex

Stripped Latex

	Wt. %			
	<u>@100 degrees C.</u>	<u>@125 degrees C.</u>	<u>@150 degrees C.</u>	<u>@200 degrees C.</u>
H ₂ O	2.74	2.97	3.42	1.38
Ethyl Chloride	nil	0.0054	1.50	3.19
Acrylic Acid	nil	0.0120	0.07	0.03
Acetaldehyde	nil	nil	0.03	0.16
Vinyl Chloride	nil	0.0033	0.01	0.01
Aromatics	nil	trace	0.25	0.09
Ethanol	nil	0.0063	0.38	0.43

Unstripped Latex

	Wt. %		
	<u>@100 degrees C.</u>	<u>@125 degrees C.</u>	<u>@150 degrees C.</u>
H ₂ O	2.5	2.79	0.32
Ethyl Chloride	nil	0.0030	1.86
Acrylic Acid	nil	0.0080	0.04
Acetaldehyde	nil	nil	0.21
Vinyl Chloride	nil	0.0020	0.32
Aromatics	nil	trace	0.21
Ethanol	nil	0.0060	0.33

APPENDIX II

3243

20563006

BFG03972