

TENNECO CHEMICALS, INC.

TO W.C. Champion
FROM F.W. Kanzler
SUBJECT T-315 Set-Up Batches

AT Burlington

COPY TO W. Miringoff
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bcc E. Young

In early February, another trial run of 315 resin was attempted. Again, a set-up occurred after the third batch charged.

Attached is a detailed summary by E. Young of the work performed in Burlington and the conclusions resulting from this work.

F.W. Kanzler

FWK/jst

INTER-OFFICE MEMO **TENNECO CHEMICALS, INC.**

TO F.W. Kanzler AT Burlington DATE March 19, 1975
 FROM E. Young AT Burlington COPY TO File
 SUBJECT Investigation of Set-Up Batches

I. Set-Up - December, 1974

The gelatin used in the set-up batch was submitted to General Foods for analysis to determine if the gelatin met all specifications. The results of General Foods' analysis (contained in a letter from James E. Foley, Jr. dated 1/3/75) are summarized below.

Analysis #1 is the initial analysis of the gelatin as reported to Mr. Champion on 12/16/74 by General Foods. Analysis #2 is the analysis of General Foods' retained sample. Analysis #3 is the sample we submitted to General Foods.

	<u>Sample #1</u>	<u>Sample #2</u>	<u>Sample #3</u>
bloom	275 gms	265 gms	265 gms
viscosity	52.0 mps	53.5 mps	51.5 mps
pH	4.45	4.45	4.30
ash	0.29%	0.29%	0.21%
moisture	6.85%	6.85%	7.36%

Mr. Foley went on to state that the gelatins used in this blend had a bloom range of 270 - 285 and a viscosity of 49.0 - 55.5.

General Foods also evaluated water samples we submitted for gelatin content with the following results:

reactor 10, batch 5195 - 0.14%
 reactor 10, batch 5187 and reactor 11 - 0.10%

Analysis on mother liquors were also done in the Flemington laboratories (3721), submitted by R.S. Miller and analyzed by C.W. Johnston. The Flemington analysis showed the following results:

reactor 10 - 0.15%
 reactor 11 - 0.09%
 control - 0.15%

The gelatin values between laboratories showed excellent correlation. These levels are in the range expected.

Further work at Flemington confirmed the presence of gelatin in the mother liquors and show this gelatin was qualitatively similar to the gelatin submitted. These tests also showed the mother liquors contained no significant amounts of Methocel. These results show nothing unusual in the mother liquors.

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The resin in reactors 10 and 11 were analyzed for bound acetate content which is shown as follows:

<u>Sample</u>	<u>315 Specification</u>	<u>Bound Acetate</u>	<u>Analytical Number</u>
reactor 10	13.5 - 15.5	14.3%	19399
reactor 11	-	11.5%	19407

Reactor 11 is out of spec low, most likely due to a set-up early in the reaction. Reactor 10, being in-spec, is most likely due to the reaction almost running to completion prior to set-up.

II. Set-Up - February, 1975

Since nothing unusual was found in the mother liquor - the presence of gelatin was confirmed; it was noted that there are two major differences between making copolymer in the Copolymer Plant versus making copolymer in the Homopolymer Plant. First is in agitation, the copolymer reactors agitate at 110 rpm and the homopolymer reactors at 117 rpm - the second difference is in the way the components are charged. In the Copolymer Plant, the components are "pre-mixed". In the homopolymer side, the components are added "sequentially". By "pre-mixed" we mean that the VCM, MVAc and TCE are mixed with each other prior to being charged into the reactor. By "sequential" we mean that first the MVAc is charged to the reactor, then the TCE, then the VCM. We were not able to examine the effect of different agitation on the reaction. We were, however, able to design an experiment which evaluated the differences between "pre-mix" and "sequential" charging.

Two experiments were run in the Analytical Laboratory to aid in the determination of the reason for the set-up in reactor 10. The first was a determination of the pH changes during the additions of the reaction components. The second was a bottle polymerization to determine the differences in "sequential" and "pre-mix" additions of the monomers to the reaction vessel.

A. pH Study

The pH study was run in the following manner: The demineralized water was preheated to 135°F. The gelatin and L_2O_2 were charged simultaneously. The pH was studied for twenty minutes, the TCE charged, the pH studied for ten minutes, the VAcM was charged and the pH was studied for five minutes. During the run, the temperature was maintained between 130 - 140°F. The following was the amounts of each constituent used in the synthetic reactor charge:

demineralized water	- 331 gms
gelatin (type "A")	- 0.88 gms
L_2O_2	- 0.34 gms
TCE	- 2.1 gms
VAcM	- 4.0 gms

The experiment was run in duplicate. The pH decreased steadily through the addition of TCE. Upon the addition of MVAc, the pH showed a marked increase during both runs.

B. Bottle Polymerization

Two bottle polymerizations were run; the first without TCE and the second with TCE:

1. Bottle Polymerization Without TCE

The following formulation was used during this run:

2% solution gelatin type "A"	- 80 gms
demineralized water	- 70 gms
L ₂ O ₂	- 0.1 gms
VAcM	- 12 gms
VCM	- 68 gms

Bottles #1, #2 and #3 were charged "sequentially". All of the substituents except VCM were added. The bottles were placed in the freezer overnight. The VCM was then added and the polymerization was run for twenty hours at 157°F.

Bottles #4, #5 and #6 were charged "pre-mixed". All of the substituents except VCM and VAcM were added. The bottles were placed in a freezer overnight. The VCM was added, then the VAcM, which had been chilled, was added. The polymerization was run for twenty hours at 157°F.

Results: Bottles #1 and #2 formed bb's approximately 1 cm in diameter, with some set-up resin in the neck of the bottles. The supernate was relatively clear.

Bottle #3 formed some good resin with agglomerates present. Coarse particles were also present in bottle #3. The supernate, while more turbid than #1 and #2, was less turbid than #4, #5 and #6.

Bottles #4, #5 and #6 formed good resin.

The gelatin in the supernate of these bottles was determined in the following manner: The supernate was filtered through #1 Whatman filter paper and the total solids of the filtrate was taken to be gelatin.

2. Bottle Polymerization With TCE

The following formulation was used during this run:

2% solution gelatin type "A"	- 80 gms
demineralized water	- 70 gms
VAcM	- 12 gms
L ₂ O ₂	- 0.1 gms
TCE	-0.65 gms
VCM	- 68 gms

Bottles #1 and #2 were charged "sequentially". All substituents were added to bottles #1 and #2 except VCM. The bottles were placed in a freezer overnight. The VCM was added. The

polymerization was run at 157°F for twenty hours. Bottles #3 and #4 were charged "pre-mixed".

All substituents except TCE, VAcM and VCM were added to bottles #3 and #4. The bottles were placed in a freezer overnight. The VCM was added, then chilled TCE-VAcM mixture was added. The polymerization was run at 157°F for twenty hours.

During this run, the batch was overheated to 165°F during the third hour of the run.

Results: Bottles #1 and #2 formed very coarse resin particles with a small amount of set-up resin in the neck of bottle #1. Bottles #3 and #4 contained good resin.

The supernate of bottles #3 and #4 were more turbid than the supernate of bottles #1 and #2.

The most likely reason we did not get bb's or more set-up in bottles during this run is the overheat. This overheat probably resulted in a reduction of catalyst activity. Also, based on observation of the amount of monomer vented after the runs, this second run had a lower yield than the first run, again because of the reduction of catalyst activity due to the overheat.

This experiment indicates that "sequential" addition of the monomers in the making of 315 copolymer will lead to set-ups. We think that the pH change following the addition of VAcM may affect the suspension properties of the gelatin-water solution. We recommend that a more detailed study of the effect of pH upon the suspension properties of gelatin "A" be done.



E. Young

-Attachments (3)

EY/jst

pH STUDY
SYNTHETIC 315 CHARGE

<u>Component</u>	<u>Time (minutes)</u>	<u>1st Run</u>	<u>2nd Run</u>
Gelatin "A" and I_2O_2	0	-	-
	1	4.43	4.20
	2	4.42	4.19
	3	4.42	4.18
	4	4.42	4.18
	5	4.42	4.17
	6	4.41	4.17
	7	4.40	4.17
	8	4.40	4.17
	9	4.40	4.15
	10	4.39	4.15
	11	4.39	4.14
	12	4.38	4.12
	13	4.38	4.12
	14	4.35	4.12
	15	4.35	4.12
	16	4.33	4.12
	17	4.32	4.11
	18	4.31	4.10
	19	4.30	4.10
	20	4.30	4.10
TCE	0	-	-
	1	4.30	4.10
	2	4.28	4.08
	3	4.23	4.05
	4	4.21	4.03
	5	4.20	4.02
	6	4.19	4.02
	7	4.18	4.02
	8	-	-
	9	4.18	4.01
	10	4.16	4.00
VAcM	0	-	-
	1	4.30	4.12
	2	4.30	4.18
	3	4.30	4.18
	4	4.30	4.15
	5	4.29	4.15
	6	-	4.12

E. Young
3/18/75

GELATIN DETERMINATION
BOTTLE POLYMERIZATION - RUN A

<u>Bottle Numbers</u>	<u>Gelatin (%)</u>
1	1.07
2	1.09
3	1.10
4	1.70
5	1.82
6	1.60
$\bar{x}$, 1, 2, 3	1.08
$\bar{x}$, 4, 5, 6	1.71

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3/18/75

