B. F. Goodrich Chemical Company
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PREVENTION OF RESIN BUILD-UP ON THE SURFACE OF THE REACTORS IN PVC POLYMERIZATION

By

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PREVENTION OF RESIN BUILD-UP ON THE SURFACE OF THE REACTORS IN PVC POLYMERIZATION

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In a long and continuing search to find some way to reduce or eliminate resin build-up on the walls of the PVC polymerizers, magnesium oxide and/or magnesium hydroxide, at very low levels, has been found to be effective. It appears now that the hydroxide is probably the active ingredient. About a dozen charges have been run in the 15 gal. and 1-75 gallon polymerizers under various conditions and levels of MgO and $Mg(OH)_2$ ranging from 2500 to 156ppm. All results with 625 ppm or more have been consistently good.

In the most recent charge, with 1800 ppm of magnesium hydroxide, the reactor was almost completely clean. When it was rinsed with water all resin flushed into the blow down tank except 34 grams (out of 360 lbs). The reaction time was six hours (10 is normal) for 73% conversion. The resin appears to be slightly course.

Conclusions

Milk of magnesia is recommended as an effective, yet gentle, ingredient for eliminating build-up in a reactor; causing no harmful side-affects, when used according to directions.

pH

Originally, the addition of magnesium oxide to a polymerizer to prevent build-up was based on the theory that it would neutralize all of the HCl which is normally split out, maintain a high pH and thereby eliminate the adhesion to the polymerizer walls. It proved to be a terrific buffer and it does eliminate build-up on the walls of the polymerizer but, apparently, not because of the high pH. Charges with 2500, 1250, 625, 312 and 156 ppm MgO (based on the monomer) have been run. The pH was almost identical in every case. They were about 10.5 pH before polymerization and 10.0 pH after polymerization. The one with 156 ppm MgO had as much build-up as the control yet the pH was 10.0 The 312 ppm was low, but more than the other charges. The ones with 625 ppm and higher had very little and it was not tightly bound. At present, it appears that 625-1250 ppm will be the optimum amount for the elimination of build-up in the polymerizers.

Magnesium oxide was chosen because it is inexpensive, non-toxic, and previous work had shown that it would improve stability without causing haze in transparent films.

Magnesium hydroxide has similar properties and is apparently more effective in preventing build-up. It will be completely evaluated as soon as possible.

SURFACE EFFECT

Since the high pH does not explain the prevention of build-up, it is now believed that the MgO/Mg(OH)$_2$ slurry forms a molecular coating on the surface of the stainless steel walls. Furthermore, it is theorized that the part in solution is not effective and that a quantity sufficient to coat the walls must be added over and above the amount which goes into solution. When 156 ppm MgO was added, it all went into solution in the water and was ineffective.

After running five charges with MgO, one was run with none and the build-up was one-fifth the control indicating possible surface effect. A stainless steel strip was immersed in a MgO slurry for 16 hours and then mounted in a production polymerizer. It had very little build-up for two charges. After six charges it had normal build-up. This test will be repeated and the strip removed after one charge.

BUILD-UP ON POLYMERIZER WALLS

	MgO Added	Grams Build-up
175 gallon poly. control	0 ppm	1600
" " " "	2500 "	128
" " " "	1250 "	245
" " " "	625 "	135
" " " "	312 "	480
" " " "	156 "	1400
" " " "	0 "	315*
" " " "	1250 "	1500**
" " " "	1800 $Mg(OH)_2$	34

* This charge was run in the same polymerizer after the preceding four charges which contain magnesium oxide. Perhaps this is the reason for the low build-up.

** This charge was run with "Maglite D", a cheap inactive rubber grade MgO, which obviously did not work.

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POLYMERIZATION CYCLE

In the above mentioned series, the times to blow-down have ranged from 15-20 hours which is 50% to 100% longer than the control. A charge with double the IPP catalyst came down in six hours and appears to be normal. (It had 1/8 pt. magnesium hydroxide. It is being repeated with magnesium oxide.) It is very encouraging that the polymerization rate responded to increased catalyst.

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It should be easy now to adjust to desired cycle time, but some increase in catalyst level will be necessary.

PARTICLE SIZE

All of the charges in the above mentioned series produced coarse resin. The coarseness seemed to be independent of the amount of MgO added. It was suspected that the MgO was reacting with the "tween" in the "Elvanol-tween" emulsifier system. A charge was run with all Elvanol and particle size appears to be about normal, but an increase in the emulsifier level is necessary. In a well buffered system, Elvanol alone may be satisfactory.

CONVERSION

The percent conversion with magnesium oxide in the polymerizer has been about normal even when the cycles were longer. The last charge with double IPP went to 73% in six hours.

MOLECULAR WEIGHT

The inherent viscosity apparently is unaffected by the presence of magnesium oxide in the polymerizer.

103EP	- Specification	- 96
103EP	- 175 gallon control	- 96
103EP	- 175 gal. + 1250 ppm MgO	- 95

ELECTRICAL INSULATION RESISTANCE

This property was determined by George Small's Electrical Group by compounding the resins from the 175 gallon polymerizer into a plasticized 2042 electrical recipe. It was extruded onto wire, immersed in water overnight and run by their standard test procedure.

		MgO Added	Meg-ohms/ 1000 ft.
103EP Production	- control	0	2920
103EP 175 gallon poly.	- control	0	3780
" " " "		1250 ppm (on mill)	3780
" " " "		625 " " "	4330
" " " "		1250 " (in poly)	4760
" " " "		625 " " "	2660*
" " " "		312 " " "	4650
" " " "		156 " " "	5320

These data indicate that MgO added in the polymerizer may actually improve insulation resistance.

* No explanation for this low value unless it was contaminated in compounding.

OVEN HEAT STABILITY @ 450° F.

Earlier work had shown that very small amounts of magnesium oxide added to a batch on the mill significantly improves the stability of tin stabilized compounds. It is more effective and more efficient when added in the polymerizer.

Vynaloy 350 recipe - with 4 parts tin stabilizer -

	Parts MgO	Time in minutes to black
103EP - Production control	0	6
103EP - 175 gal. control	0	8
" " " "	156 (in poly)	11
" " " "	312 " "	12
" " " "	625 " "	16
" " " "	1250 " "	18
" " " "	1250 (on mill)	14

Vynaloy 350 recipe - with 2 parts tin stabilizer -

	Parts MgO	Time in minutes to black
103EP - Production control	0	1
103EP - 175 gal. control	0	3
" " " "	156 ppm (in poly)	5
" " " "	312 " " "	6
" " " "	625 " " "	9
" " " "	1250 " " "	11
" " " "	2500 " " "	9
" " " "	1250 " (on mill)	8

It appears that 1250 ppm added in the poly gives the maximum increase in stability in this system. It is interesting to note that the 2500 ppm hurt the stability.

DYNAMIC THERMAL STABILITY

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These results were run by John Whitney's Group using a Vynaloy 350 recipe with 2 parts tin stabilizer (same as the one used for oven stability above).

	MgO added in poly.	Time
103EP - 175 gal. poly control	0	18 min. 53 sec (Av)
103EP - 175 gal. "	156 ppm	25 min. 20 sec
" " " "	312 "	25 min. 50 sec
" " " "	625 "	26 min. 30 sec
" " " "	1250 "	27 min. 45 sec

It is interesting that only 156 ppm MgO added in the polymerizer increased the D.T.S. about 34%. 1250 ppm increased the time 47% over the control.

RESIN CHARACTERIZATION

Samples of the resins polymerized with various levels of MgO have been given to Ed Collins. No report as yet.

ANALYTICAL EXAMINATION

Samples of the resins polymerized in the presence of magnesium oxide have been examined by Lin Crider's Group. They report the magnesium is not chemically bound, but it is very intimately dispersed. It was impossible to throw it out of solution with a normal centrifuge. However, they were able to separate it with an ultra high centrifuge. In solution, the control sample seemed to have more gelled particles.

ASH

The amount of magnesium oxide remaining in the resin varies widely according to the ash results obtained by the Analytical Group. The percentage of the amount charged ranged from 16 to 50%. Additional data will be gathered on future charges.

FISHEYES

No information yet. However, it has previously been established that the well cleaned polymerizers reduce the number of gelled resinous particles.

BULK DENSITY

Only one sample run. It will be further investigated as soon as the process is under control.

	Bulk Density gms/cc
103EP F74 Specification *	.55 - .60
175 gallon poly. control *	.55
15 " " all Elvanol - 1250 ppm MgO	.30

It is not known whether the all Elvanol or magnesium oxide caused the low bulk density. (Probably the Elvanol). Do not know yet whether this will be a serious problem..

* Elvanol-tween with no magnesium oxide.

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POROSITY

Only one sample run. It will be further investigated as soon as process is under control. It is not known yet whether the high porosity is good or bad.

BRABENDER FUSION TIME

No data as yet.

ANGLE OF REPOSE

No data as yet.

STATISTICAL STUDIES

We have now run enough charges to find out what factors influence the polymerization in the presence of magnesium oxide and hydroxide. A statistically designed series has been set up, with the help of Bob Bowles and Claude Brunot, to optimize polymerization conditions.

ECONOMICS

High quality magnesium oxide is about 75¢ per pound whereas the same quality magnesium hydroxide is about 25¢ per pound. Obviously, we would like to use the hydroxide. Also, the hydroxide is a more reliable, uniform quality product. We have only run one charge with the hydroxide and it looked good. In any case, at 1250 ppm the cost is insignificant.

POTENTIAL COST SAVINGS

It is difficult to arrive at an actual figure, but if we can succeed in eliminating polymerizer cleaning completely, it could save several million dollars per year in labor and lost production time.

OTHER APPLICATIONS

To date, all of the work has been done with 103EP pearl resin. It is expected to work equally well with the acetate, vinylidene, and propylene copolymers. It may also be useful in bulk and/or continuous polymerizations.

The use of magnesium oxide and/or hydroxide should be investigated in latex and rubber polymerizations if build-up on the polymerizer walls is a problem.

PRODUCTION UNIFORMITY

The unusual capacity of magnisium oxide and/or hydroxide to maintain a constant pH of 10.0 throughout the reaction may tend to level out operational variables such as loss of vacuum, changes in the water, seasons of the year; resulting in more uniform quality.

LEGAL STATUS

A patent record, covering the use of magnesium oxide and hydroxide to improve heat stability and to eliminate build-up in polymerizers has been written. It has been discussed twice with J. Hughes Powell and additional, specific data is being gathered so patent application can be made as soon as possible.

SCALE-UP

Since charges with magnesium compounds added in the polymerizer require more catalyst and more emulsifier than standard recipes, additional data will be needed before going to larger equipment. The surface volume ratio is much less in production polymerizers and this probably will change the amount of magnesium compound needed. Also, a thorough evaluation of all resin properties must be made to make sure no unforeseen difficulties develop.

Note:

All polymerization studies have been supervised by A. A. Etter. His contribution is gratefully acknowledged.

C. E. Parks

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