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TENNECO PLASTICS DIVISION
Research and Development Department
Process Engineering Section

Project No.: 70-001
Date: April 23, 1969

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TITLE: MVC Monomer Evaluation
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DIGEST

A study of monomer quality and its effects on reaction kinetics was made during February and March, 1969. It was estimated from the study that due to the varying and excessive impurity levels in Tenneco monomer, potential profits are being lost at an annual rate of $121,000. It was recommended that Tenneco Hydrocarbons take steps to improve and insure the monomer quality.

RECOMMENDATIONS

1. Tenneco Hydrocarbons should take the appropriate steps to improve and insure monomer quality.

2. Study the heavy end impurities that are found in the PPG monomer, such that identification and quantitative levels can be determined. The effects that these impurities have on reaction kinetics and resin properties should also be studied.

CONCLUSIONS

1. Two competitive monomers were evaluated during the study. In general, the Allied monomer (free of light and heavy end impurities) gave better kinetics and resin properties compared to Tenneco monomer, especially when recovered monomer was used. PPG, on the other hand, (free of light end impurities but containing substantial quantities of heavy end impurities) gave kinetics and resin properties very similar to Tenneco.

2. No direct correlation could be found between virgin monomer quality and suspension resin quality. However, longer reaction times were experienced in the homopolymer plant due to highly concentrated impurity levels in recovered monomer.

3. Longer reaction times were experienced in the Plastisol process due to variable and excessive impurity levels in the virgin monomer. This translated to an annual loss in production of 1.7M pounds.

DISCUSSION

During February and March, a study was undertaken to evaluate the effects of Tenneco monomer impurities on costs, reaction kinetics and resin properties. Both the Allied and PPG monomer evaluations took place during this period.

It should be noted that in most cases, cause and effect relationships, discovered by this study, could not always be substantiated with sufficient statistical data. As in the case for most in process studies, trends became the major response. For this study, laboratory data was also used to substantiate the plant data.

A. Monomer Quality

Three unsaturated impurities; Allene, Methyl Acetylene, and 1,3 Butadiene were monitored. Their concentrations were determined by graphing Houston's GC analysis of the monomer tank car, based on the day it was unloaded into the monomer storage tank (Figure 1). This is a reliable technique since good correlation has, for the most part, been shown between Houston and Burlington GC analysis (Ref. 4).

Despite the considerable spread in the data, the average Allene and 1,3 Butadiene concentration appeared to peak, around the latter part of February, to 120-150 ppm and 7-10 ppm respectively. The average Methyl Acetylene concentration did not appear to vary.

GC analysis of Allied monomer indicated it was "clean" of Tenneco type impurities (See Figure 6). It did, however, contain 150 ppm of Methyl Chloride (Ref. 2), (the high level is peculiar to oxychlorination process). Since Methyl Chloride is a saturated hydrocarbon, it does not appear to be as reactive or affect the polymerization reaction as do Allene or 1,3 Butadiene.

GC analysis of PPG monomer indicate that it was also clean of light end impurities. However, heavy end contaminants were detected but not identified. The Methyl Chloride level was 35-50 ppm, much less than Allied.

B. Polymerization Performance

From the Allied monomer evaluation, the average reaction times of 225/16R batches were plotted as a function of the average amount of recovered monomer charged per batch (Figure 5). The Tenneco reaction times increase at a greater rate than Allied as more recovered monomer is charged. This is due to the detrimental effects of concentrated light end contaminants. Consequently, a 225/16R homopolymer reaction would run about 20 minutes

less if clean monomer were used. This directly translates to a 1M pound increase in productivity per year, if the extra reaction time were used to make 225/16R. This is equivalent to an annual increase in profits of $28,000. Here again, an equivalent incremental capital investment of $110,000, (based on 11¢/lb. investment) would be required to increase the capacity of our present plant to this level.

It is important to note that 5% to 20% of our monomer charged is recovered monomer. In order to maximize profits, this recovered monomer must be used. In recovered monomer, light end impurities will concentrate 7 to 50 times their original level. (Saturated hydrocarbon impurities concentrate much more than unsaturated hydrocarbons). It is suspected that the double and triple bonded impurities react with initiator radicals faster than vinyl chloride, hence they are detrimental to the reaction. If Houston could produce virgin monomer such that the recovered monomer that was generated has the quality of our present Tenneco MVC, then the cost burdens outlined in this report could become additional profit.

Productivity sacrifices were also noted in the dispersion resin plant. A recent study of monomer quality versus plastisol reaction times by E. J. Hourihan (Ref. 1) states that a correlation appears to exist between a decreasing Allene concentration (from 100 to 50 ppm) and a decreasing reaction time in plastisol (1.5 hours less). This translated to an annual savings of $82,000. This figure included the net profit due to an additional 720,000 pounds of resin that could be made. Here again, an equivalent capital investment of $160,000 (based on 22¢/lb.) would be required to bring our present plant up to this capacity, given that the Allene level in Tenneco monomer is at least 100 ppm.

C. Resin Quality

Homopolymer (225/16R) and copolymer (315) resin quality was monitored in an effort to define trends which would correlate with monomer quality. Figures 2 and 3 show plots of dry blend, +100 mesh screens for copolymer (315). Chronologically superimposed on the charts were events which might affect production quality. During the Allied evalution, 315 copolymer lots did not require the addition of soda ash for improving the light absorbance and heat stability. However, soda ash was needed when Tenneco MVC was used. This is equivalent to an annual savings of $3800.

When recovered monomer generated in the plastisol process was used in the copolymer plant rather than the homopolymer plant, a favorable lowering of gels and dry blend time occurred in 225/16R homopolymer lots (Figure 2). The high levels of light

end contamination are suspected to have an adverse effect on homopolymer resin properties. Based on the amount of 225/16R homopolymer dispositioned as II grade due to high gels and dry blend times and a 1.54 per pound difference in selling price, $7800 lost in profits last year. No analogous trend was found in copolymer lots because of the high degree of scatter in the data.

Figure 4 depicts the E-grade lots from homopolymer and copolymer and the reason for failure. The same events as above were superimposed. In general, the same trends are found.

D. Summary of Cost Savings

Based on this study, an annual rate of $121,000 in lost production has been attributed to poor monomer quality; virgin and recovered. 1.7M pounds of annual production is being sacrificed due to the high level of impurities in the virgin and recovered monomer and its detrimental effect on reaction kinetics. This translates to an equivalent incremental capital expenditure of $270,000 to bring the plant up to this capacity. It is also interesting to note that the above losses constitute a cost burden of 0.061¢/pound of monomer (based on 200M pounds usage annually).

	Savings and Extra Profit	Equivalent Incremental Capital Invest.	Savings & Extra Profit /Lb. Monomer used
1. Possible yearly savings by not using soda ash in copolymer resins	$3800		2×10^{-3}¢/lb.
2. Possible extra profit due to shorter reaction times in Plastisol plant based on monomer study.	$82,000	$160,000	4.1×10^{-2}¢/lb.
3. Possible increase in profits due to less E-grade 225/16R, generation if monomer quality were better	$7800		3.85×10^{-3}¢/lb.

	Savings and Extra Profit	Equivalent Incremental Capital Invest.	Savings & Extra Profit /Lb. monomer used
4. Possible extra profit due to reduced manufacturing cost and shorter reaction times in homopolymer plant	$28,000	$110,000	1.4×10^{-2} ¢/lb.
	$121,000	$270,000	6.1×10^{-2} ¢/lb.

The above cost burdens could become additional profits if Tenneco Hydrocarbons would take the appropriate step to improve and insure good quality monomer. In effect, the majority of our problems, which are related to recovered monomer, are directly related to virgin monomers. For example, if Houston could reduce the Allene level in the virgin monomer from 100 to 5 ppm, this would translate to a reduction from 1500 to 75 ppm in the recovered monomer. In essence, the recovered monomer would be of equivalent quality to our most recent Tenneco virgin MVC.

An increasing amount of effort is being spent on studying monomer quality and its effects on kinetics and resin properties.

It is estimated that $67,000 will be spent this year in this area. If good monomer quality were obtained, this appropriation could be used to study new and more profitable areas.

There are some aspects of monomer quality which are very difficult to translate into savings. For instance, in the plastisol unit, varying monomer impurity levels have been known to cause variable reaction times and resin properties. As a result, the plant is operated below design capacity. Some lots are out of specification which require special dispostion by Customer Service Laboratory.

G. W. Leach

GWL/rjl

Attach.

REFERENCES

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2. Inter-office Memo, Gas Chromatographic Analysis of Light End Impurities in Competitive MVC, to H. B. Carr from F. W. Kanzler, dated March 27, 1969.

3. E Grade Dispositions, 1/68 - 3/69.

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5. Inter-office Memo, VCM - Status Report, to M. W. Williams from H. B. Carr, dated November 12, 1968.

6. Inter-office Memo, VCM, to H. B. Carr from E. Farber, dated December 6, 1968.

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