

H. B. Cair

Houston
E. C. Report

70-001

INTER-OFFICE COMMUNICATION

TENNECO HYDROCARBON CHEMICALS

July 31, 1969

TO: Laboratory Files
FOR: D. J. Cleckley
FROM: G. R. Harvey
RE: Calibration change for VCM Light Ends Analysis

SUMMARY

A sample of our VCM from a hold tank was analyzed by chromatography for the light hydrocarbons by several laboratories. The results indicate the THC laboratory analyses have been high by a gross amount. On Friday, August 1, 1969, it is planned to change the THC factors to bring them in line with the other laboratories. The sample analyzed by the laboratories will be retained to routinely calibrate the chromatograph. In addition a gas blending kit has been purchased so that blends can be made to recheck the standard.

INTRODUCTION

Propadiene, methyl acetylene and 1,3 butadiene are impurities of our vinyl chloride monomer product which must be kept below the specification level required by Tenneco Plastics Division. The impurities are in the PPM range. There have been disagreements in chromatographic analyses for these components among laboratories, both inside and outside the company.

The economic consideration of the acceptance or rejection of an entire car load of product has required that the analysis differences be resolved immediately.

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DISCUSSION

As a basis for comparing analyses among laboratories, and in order to check reproducibility of our analyses, a cylinder of hold tank product was collected. Samples from this cylinder have been analyzed by our laboratory, the Tenneco Plastics laboratory and by three laboratories of vinyl chloride producers outside the company: Dow Chemical Company, Freeport; Pittsburgh Plate Glass Company, Lake Charles and Continental Oil Company, Lake Charles. The results are tabulated in Table I.

A comparison of the results shows very good agreement among the outside laboratories. Our laboratory reported answers much higher than the outside companies -- five times higher in the case of propadiene. Tenneco Plastics was in closer agreement with the outside laboratories but was two and one half times higher for propadiene.

The calibration factors for the THC laboratory analyses were derived in the Fall of 1968 and based on Dow's analyses of various samples. The expedient of taking Dow's analyses was used because it was believed they would be satisfactory. Tenneco had just become aware of the importance of these impurities while Dow was experienced in vinyl chloride monomer production. We did not make a primary standard.

In the THC method of analysis, a liquid sampling valve is used to introduce the sample into the chromatograph. The separation is on a tributyl phosphate column at 160 to 200. Components are detected by hydrogen flame ionization. Peak areas are calculated by multiplying the height by the width at half height. These in turn are multiplied by the respective calibration factors. The calibration factors have not been adjusted since originally determined, except as noted below for propadiene.

There are several possible reasons why sensitivity of the THC chromatograph could have changed: (1) Column oven cooling is not thermostatically controlled, and so the temperature can change with room temperature change. (2) A faulty electrometer cable was recently changed. (3) Carrier flow rate is difficult to measure and so is not checked frequently. (4) Human error has been observed in measuring the relatively narrow peak widths.

I personally visited each of the outside laboratories to deliver the samples. Mr. Ray Goudreau was the chemist directly involved at Dow during the visit to Freeport on July 15, 1969. Messers Jack Skaggs and Rodney Webb at Dow were also interested in the problem. Mr. Buddy Hann was the host at Pittsburgh Plate Glass with Mr. Bob Pertuit giving his full attention to our

sample. Mr. Ed Peveto was the chemist at Continental Oil. Messers Pertuit and Peveto were taken to lunch during the visit to Lake Charles on July 17, 1969.

The most obvious observation was that each laboratory used a different method. The only common points were gas sampling and flame ionization detection.

Dow vaporized the sample across a heated valve, Pittsburgh Plate Glass across an unheated valve and Conoco across capillary tubing immersed in oil at room temperature. Dow and PPG sampled with a commercial valve while Conoco used a syringe. Dow did not know their sample size, PPG used 0.5ml and Conoco 5.0 ml. Dow separated on a tributyl phosphate column at 20C thermostatically controlled; PPG separated on an undisclosed column with programmed temperature beginning at 50C; Conoco separated on bis [2 - (2 methoxyethoxy) ethyl] ether at room temperature. Dow measured peak height, PPG measured peak area as we do and Conoco measured peak area electronically by an Infotronics integrator. Dow corrects their calibration factors once per week by running a standard blend, as does Conoco once per shift. PPG does not use a standard blend but instead accounts for all components and normalizes to 100%, using relative response factors.

CONCLUSION

The analyses of the outside laboratories would appear to be approximately correct because of the remarkable, uncollaborated agreement using diverse techniques. If this is so, the THC laboratory should correct its method to be in agreement with the others.

RECOMMENDATION

Unless reasons are presented otherwise, the VCM analysis method of calculation will be changed Friday, August 1, 1969 to bring the analyses in agreement with the outside laboratories. The analysis of each component will be reduced by the ratios shown in Table I between the average analysis of outside laboratories and the THC laboratory analysis. An exception is propadiene factor which has already been reduced by one third on July 23, 1969, based on preliminary data. The propadiene reduction on August 1 plus the previous one third reduction will equal the ratio shown in Table I. A new scale will be provided for the VCM Control Room process analyzer.

TABLE I

COMPARATIVE ANALYSES, VCM STANDARD BLEND #2

Hold Tank Sample, July 11, 1969

<u>LABORATORY</u>	<u>THC</u>	<u>Tenneco Plastics</u>	<u>Dow</u>	<u>PPG</u>	<u>Conoco</u>	<u>Average, outside labs</u>	<u>Ratio, (outside labs)/THC</u>
DATE ANALYZED July, 1969	18-22	23	15	17	17		
Propane	3	2	0.6		0.5	0.6	0.20
Propylene	11	11	1.9		1.8	2.	0.18
Isobutane	4	2	1.		0.8	1.	0.25
Propadiene	107	49	19.7	17.6	18.6	19.	0.18
Butane	3	< 1	0.8			0.8	0.27
Butene - 1	3	< 1	0.8			0.8	0.27
Methyl acetylene	8	2	2.		1	1.6	0.20
Methyl chloride	18	9	12	9	7	9.	0.20
1,3 Butadiene	9	3	4	3	3	4.	0.44

All data on ppm by weight.

Gary

These are the findings
reported in a memo I
can't find but written ~1967

The normal % conversion
after shock is ~10% so
that a 400% increase means
~~40~~ 50% conversion

Edcott

JUL 25 1969

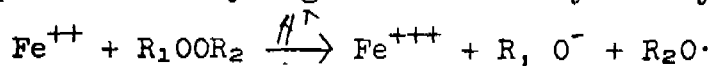
COP-11

An analysis of Tables I and II show the following:

In those systems employing 0.050 phm Lupersol 11 as the catalyst, there is no noticeable change in the initial polymerization kinetics which is ^{when} ~~dependent on the~~ ^{source} ~~type~~ of water used in making up the suspension ^{was varied between} ~~28~~, distilled, cold ^{or} ~~and~~ hot demineralized water, and well water ~~were used~~. The conductivity of the distilled and deionized waters were about the same (0.5--2.0 ppm as NaCl) while the conductivity of the well water ~~and~~ exceeded our scale reading of 20 ppm as NaCl. (I am informed that the conductivity of well water is about 2,000 ppm as NaCl. The metals present in well water must consist of less than 5 ppm Fe⁺⁺ according to our results. In all probability, the major impurities in well water are probably Ca⁺⁺, Mg⁺, Na⁺, K⁺ and/or other ~~monovalent~~ ^{having only one valence} metals.) ^{scale}

It should be noted that the use of recovered, rather than virgin, MVC results in a slower kinetic rate of polymerization.

Upon the addition of Fe⁺⁺, the degree of conversion ⁱⁿ ~~after~~ two hours ~~begins to~~ accelerate markedly. The addition of one drop of concentrated HCl to the suspension system to lower the pH. from about 6 to 2.5 also increases the percent conversion when low amounts of Fe⁺⁺ are added since the presence of hydrogen ions usually catalyses a Redox system.



The presence of about 150 ppm Fe⁺⁺ (added as FeCl₂) drastically increases the percent conversion 4--5 times that of the control. Increasing the Fe⁺⁺ level to 500 ppm does not appear to increase the degree of conversion over that noted when 150 ppm Fe⁺⁺ is added.

The addition of Fe⁺⁺⁺ (rather than Fe⁺⁺) has a much less marked effect on the polymerization kinetics. The increase in kinetic rate noted when Fe⁺⁺⁺ (as FeCl₃) is added can be attributed to a ^(slight) catalytic effect in the decomposition of Lupersol 11 and/or trace impurities of Fe⁺⁺.

It must be noted that the use of Fe^{++} (5—500 ppm) results in a thin coating appearing on the sides of the coke bottles which is fairly easy to clean off by scrubbing. Such a coating is not evident when Fe^{+++} is the additive. Also, the addition of Fe^{++} results in clumping of the resin particles; the higher the Fe^{++} level, the more difficult it is to break such clumps although no really extremely hard-to-break aggregates are formed. The higher the Fe^{++} level, the darker is the color of the dried resin.

Addition of Fe^{+++} does not cause a film to be formed on the inner surface of the Coke bottle as does the use of Fe^{++} . In addition, clumping is not evident in those systems where Fe^{+++} was used, but the color of the dried resins wherein Fe^{+++} was added are slightly darker than those having equivalent amounts of Fe^{++} in the polymerization formula.

Table II indicates there is no change (other than a darkening in the dried resin) in the degree of conversion after the first few hours when lauroyl peroxide replaces Lupersol 11 as the catalyst.

TABLE I

Effect of Various Ingredients on the Percent Conversion of Vinyl Chloride After Two Hours Reaction Time Using 0.050 phm Lupersol 11 as Catalyst 133°F.

<u>Formulation Changes</u>	<u>Δ % Conversion</u>
pH 2.5	--
Cold Deionized H ₂ O	--
Cold Deionized H ₂ O + Recovered MVC	(-5%)
Well Water	--
Well Water + Recovered MVC	(-5%)
Recovered MVC	(-5%)
5PPM Fe ⁺⁺ (pH = 5.7)	+5%
5PPM Fe ⁺⁺ + Recovered MVC	--
5PPM Fe ⁺⁺ + Recovered MVC + Cold Deionized H ₂ O	--
5PPM Fe ⁺⁺ (pH = 2.5)	+10%
5PPM Fe ⁺⁺ (pH = 2.5) + Recovered MVC	+5%
5PPM Fe ⁺⁺ (pH = 2.5) + Recovered MVC + Well Water	+5%
5PPM Fe ⁺⁺ (pH = 2.5) + Recovered MVC + Well Water + 0.5PPM Ionol	+5%
5PPM Fe ⁺⁺ (pH = 2.5) + 0.5 PPM Ionol	+10%
50 PPM Fe ⁺⁺	+100%
50 PPM Fe ⁺⁺ (pH = 2.5)	+150%
150 PPM Fe ⁺⁺	+400--550%
150 PPM Fe ⁺⁺ (pH = 2.5)	+400--550%
500 PPM Fe ⁺⁺	+400--550%
500 PPM Fe ⁺⁺ (pH = 2.5)	+400--550%
500 PPM Fe ⁺⁺ + Recovered MVC	+300--400%
500 ppm Fe ⁺⁺⁺	+25%
500 ppm Fe ⁺⁺⁺	+50%
500 ppm Fe ⁺⁺⁺ (pH 2.5)	+50%

TABLE II

Effect of Various Ingredients on the Percent Conversion of Vinyl Chloride of Vinyl Chloride After Two Hours Reaction Time Using 0.185 phm L_2O_2 as Catalyst at 133°F .

<u>Formulation Changes</u>	<u>Δ % Conversion</u>
pH = 2.5	--
50 ppm Fe^{++}	--
150 ppm Fe^{++}	--
500 ppm Fe^{++}	--
500 ppm Fe^{++} (pH = 2.5)	--
50 ppm Fe^{++}	--
500 ppm Fe^{++}	--
500 ppm Fe^{+++} (pH = 2.5)	--