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MANUFACTURING CHEMISTS ASSOCIATION

1825 CONNECTICUT AVENUE, N.W. WASHINGTON, D.C. 20009 (202) 483-6128

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July 15, 1974

R. N. WHEELER, JR.

TO: Technical Task Group on Vinyl Chloride Research

SUBJECT: Proposals for Research on Atmospheric Chemistry
of Vinyl Chloride

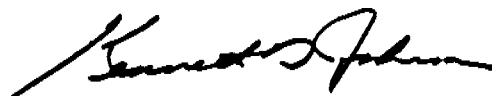
Gentlemen:

At the request of the Research Coordinators made in connection with preparations for the April 2nd briefing of the EPA delegation on vinyl chloride, I have informally solicited known operators of smog chambers for proposals to investigate the atmospheric reactions that may influence the rates and routes of destruction of vinyl chloride released into the atmosphere.

Attached hereto are copies of proposals that have been submitted by Battelle and Lockheed. Please review them and be prepared at our next meeting to offer your evaluation of their appropriateness for industry support and their technical competence.

The results of such research may be of critical importance as industry develops its position on any limitations on vinyl chloride discharges that EPA may propose pursuant to the authority granted them in section 112 of the Clean Air Act.

Sincerely,



Kenneth D. Johnson, Ph.D.
Secretary

Technical Task Group on
Vinyl Chloride Research

KDJ/mb

Enclosures

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Lockheed

MISSILES
& SPACE
COMPANY

June 27, 1974

MANUFACTURING CHEMISTS ASSOCIATION
1825 Connecticut Avenue, N.W.
Washington, D.C. 20009

Attn: Kenneth D. Johnson, Ph.D.
Assistant Technical Director
Air Quality

Dear Ken:

It is a pleasure to submit for your consideration an outline of a program to determine the atmospheric photochemistry of vinyl chloride. By using the Lockheed smog chamber with its xenon arc lamp illuminator, the best simulation of ground-level ultra-violet so far applied to photochemical testing will be used in your study. Other desirable features of the Lockheed chamber as applied to your needs are the all Pyrex-Teflon construction of the chamber, the demonstrated reproducibility of the facility, the low background reactivity, and the fact that we can clean the chamber by vacuum off-gassing. These features and the dedicated analytical instrumentation are discussed in the Fact Sheet that I have enclosed. Just down the hall from the smog chamber is the Biotechnology Analytical Chemistry Laboratory which includes additional instrumentation that will be used in the study:

Hitachi-Perkin Elmer RMU 6D
Mass Spectrometer equipped for tandem GC operation
Hewlett-Packard 7620A Gas Chromatograph
Perkin-Elmer Model 531 IR Spectrometer (10 meter cell)
F&M Model 810 and Model 700 Gas Chromatographs (several)

For planning purposes, we estimate that the 28 test program can be conducted and a final report submitted in five months after receiving your go-ahead. We estimate that about 70 man-weeks of effort would be required for the program, which would be billed at about \$1000 per man-week. Materials and other charges would be billed at cost and are estimated at less than \$20,000. In other words, for budgetary planning purposes, you could estimate a total price not to exceed \$90,000 for the study, on the basis of a time-and-material arrangement. Call me if you have any questions or comments.

Sincerely,

LOCKHEED MISSILES & SPACE COMPANY

RJ
R. J. Jarre, Project Director
Environmental Systems
Biotechnology, Orgn. 56-20, B/151

RJJ:nl
Encl.

A GROUP DIVISION OF LOCKHEED AIRCRAFT CORPORATION

SUNNYVALE, CALIFORNIA

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ATMOSPHERIC PHOTOCHEMISTRY OF VINYL CHLORIDE

Little data is available at present on the atmospheric photochemistry of vinyl chloride (VC). Lockheed Missiles & Space Co. (LMSC) proposes to perform a series of tests to determine the behavior of the VC/Oxides of nitrogen (NO_x) system, with and without hydrocarbons present. The test program is planned to elucidate the photochemical behavior under simulated atmospheric conditions, using the Lockheed Smog Chamber Facility.

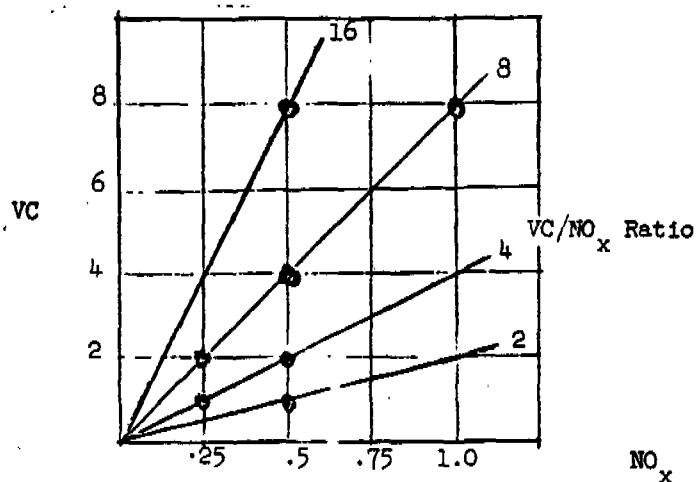
Test Program

Each test consists of cleaning the chamber; charging the reactants; turning on the solar illuminator; and monitoring the concentration changes. The following species are determined: VC, NO, NO_2 , Ozone, and Hydrocarbons (as appropriate). Other possible reaction products will be investigated. Reference test conditions are: 95°F chamber temperature, 53°F dew point (25% relative humidity), light intensity of 0.4 min.^{-1} as measured by nitrogen dioxide photolysis (k_d). All tests will be duplicated.

1. VC/ NO_x Tests - 14 Tests

The VC/ NO_x reaction system will be investigated at seven combinations of VC and NO_x concentrations, chosen to facilitate subsequent data manipulation. A preliminary selection is:

VC	NO_x	VC/ NO_x Ratio
8 ppm	0.5 ppm	16
8	1	8
4	0.5	8
2	0.25	8
2	0.5	4
1	0.25	4
1	0.5	2



LOCKHEED MISSILES & SPACE COMPANY

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As can be seen from the figure, this allows data to be obtained: as a function of VC concentration at fixed NO_x (vertical traverses); as a function of concentration at fixed VC/ NO_x ratio (sloping traverses); and as a function of NO_x concentration at fixed VC (horizontal traverses).

2. Hydrocarbon - VC/ NO_x System - 6 Tests

The interrelationship obtained in the system of VC/ NO_x and atmospheric hydrocarbons is of practical and theoretical interest. The hydrocarbon for such a test can range from a single representative one, such as propylene, to the 17 component mixture used by the Environmental Protection Agency. Use of a three-component mixture is planned. The three hydrocarbons, n-butane, propylene, toluene, typify paraffins, olefins, and aromatics and are each found at significant levels in the atmosphere. Each compound will be charged at 0.5 ppm C in the smog chamber, to give a 1.5 ppm C atmosphere. The NO_x concentration will be 0.5 ppm. Two levels of VC of 1.0 and 4.0 ppm will be used. These test data will be compared to a test with no added VC. Such tests will indicate: the effect of VC upon photochemical behavior of the hydrocarbons, and the changes in VC kinetics in a hydrocarbon- NO_x atmosphere.

3. Relative Humidity Effects - 6 Tests

Effect of mixture relative humidity is not well established for hydrocarbon/ NO_x reaction systems. Such effects may be large in the VC/ NO_x photochemical system. For a selected VC/ NO_x charge, data will be gathered at chamber gas dew points of -20°F , 30°F and 75°F , in addition to the 53°F standard dew point. This yields a set of relative humidity of 1%, 10%, 25% and 50% at the chamber gas temperature of 95°F .

4. High Reactant Concentration Test - 2 Tests

To assist in identification of trace species found in the VC/ NO_x system, a photochemical test will be conducted at "high" concentration conditions, such as 48 ppm VC/3ppm NO_x . Samples for this test will be subjected to intensive chemical analysis using mass spectrographic and I-R spectrographic techniques, and a combined GC-MS analysis method.



Columbus Laboratories
305 King Avenue
Columbus, Ohio 43201
Telephone (614) 299-3151
Telex 24-5454

June 26, 1974

Dr. Kenneth D. Johnson
Manufacturing Chemists Association
1825 Connecticut Avenue, N.W.
Washington, D.C. 20009

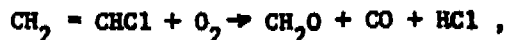
Dear Dr. Johnson:

The Fate of Vinyl Chloride

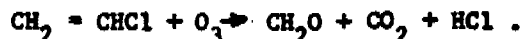
This letter will serve as Battelle's Columbus Laboratories unsolicited proposal on a study to determine the principal oxidation and reaction products of vinyl chloride in the atmosphere.

The recent concern over the possible health hazards of vinyl chloride is obviously very disconcerting, especially as regards the potential of vinyl chloride to cause serious liver damage, enlarged spleens and deleterious blood diseases, and skin eruptions. Therefore, evaluation of the potential hazards of vinyl chloride as an in-plant emission product, as well as an out-of-doors air pollutant, becomes of major concern. It is the purpose of this proposal to evaluate the stability of vinyl chloride emissions under both dark and sunlight-irradiation conditions, and to attempt to categorize all, or at least the major reaction products of vinyl chloride in the atmosphere.

Vinyl chloride is a fairly reactive organic material. For example, it polymerizes and copolymerizes very readily, which accounts for it being such a major product in plastics technology. In general, one expects vinyl chloride to oxidize with the atmosphere in the manner



or in the presence of ozone



Battelle's Columbus Laboratories has examined the smog reactivity of vinyl chloride in our large (aluminum-Teflon) smog chamber. At levels of 1 and 4 ppm (volume basis) the smog reactivity of vinyl chloride was very dependent

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on organic / NO_x ratio, more ozone being produced at the higher ratio. This early work, since it was directed to defining the smog reactivity, did not examine the fate of the vinyl chloride. Aldehyde analyses in this study, however, indicate that some 25-50 percent of the vinyl chloride was converted to aldehyde in a 5-hour irradiation period, suggesting that vinyl chloride may have a limited lifetime in sunlight atmospheres.

Another interesting feature of this initial work was the evidence of PAN, or possibly a chlorinated organic product among the smog products.

Proposed Program

Objective

It is proposed that the principal objective of this program be a definition of the major oxidation and decomposition products of vinyl chloride. It is suggested that the program first establish the extent to which formaldehyde, carbon monoxide, and hydrogen chloride can account for the removal of vinyl chloride from any atmosphere. Depending upon the ability of these three products to account for the breakdown of vinyl chloride, more detailed analysis of other species would be undertaken to help define the fate of vinyl chloride.

Experimental Program

It is proposed that this study be conducted in Battelle's two 50-cu-ft all-Teflon chambers - not in the large smog chamber. At some later time, one may desire to carry out some experiments in the large chamber to determine the extent to which the aluminum-oxide coated walls of the large chamber may influence the stability of vinyl chloride. (Recognizing that all chambers exert some type of wall effect, we have not seen any especially severe effects of our aluminum walls on sulfuric and nitric acid deposition.)

We propose that four general sets of conditions be examined in this program

100 ppm (v/v) vinyl chloride
lighted and dark

2 ppm (v/v) vinyl chloride
lighted and dark.

The above systems would be examined in relatively clean air (using our chamber air purification train) at about 50 percent relative humidity to which we would add 0.5-1.0 ppm NO_x (about 10 percent NO₂). The high concentration systems, besides providing for easier analysis, will also provide the necessary information for the role of concentration effects on the reactions of vinyl chloride. Also, if it should turn out that the chemistry and kinetics are not substantially different at 100 ppm and 2 ppm vinyl chloride, the high concentration system would allow one to collect and identify the minor products more readily.

Analyses of the major substances in this program would be as follows:

vinyl chloride	FID - G.C.
CH ₂ O	chromotropic acid method
CO	FID - G.C.
HCl	IR, wet chemical, or micro-coulometric.

Attempts to identify other products, such as PAN, chloraldehydes, and unknowns not established as yet, would be carried out by G.C., mass spectrometry, and infrared (Fourier transform analysis) as required.

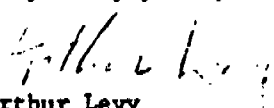
Time and Costs

Inasmuch as the importance of other than the three major products, CH₂O, CO, and HCl is not known as yet, it is suggested that this program, as proposed here, be considered as a Phase 1 study. It is suggested that this initial program be carried out over a period of 3 or 4 months at an estimated cost of approximately \$25,000. Pending the outcome of this program, one will then be in a position to ask what the health hazards of the reaction products might be, and what the importance of other environmental variables might be.

Anticipating that members of MCA may want to discuss the proposed program further, this proposal is sent as a preliminary document. After further discussions, Battelle will be pleased to submit a formal proposal and appropriate agreement forms, subject, of course, to our other commitments at that time.

We hope that this document will serve as a basis of further discussion with you and your staff. Please call me at Extension 2939 for further information.

Very truly yours,


Arthur Levy
Senior Research Leader
Chemistry Department

AL:mac

In duplicate