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Monsanto

FROM (NAME & LOCATION) Betty Gates - Organic Research Library-1700 South Second St.

DATE October 3, 1967

CC

SUBJECT Toxicity and Hazards

REFERENCE

TO : Mr. E. Wheeler
General Offices

Attached is section on Toxicity and Hazards for Tentative Process P-1465, entitled "Production of PB-702 Pigment Binder", written by M.E. Gibbs and S.M. Balaban, dated September 26, 1967, Job No. 6515.

Betty Gates

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IN-10 REV 11-65

13. Composition of the THF-H_2O Mixture

The weight percent of THF in a H_2O mixture may be found by measuring the index of refraction. The relationship between indices of refraction and composition is shown in Figures 10 and 11.

14. Composition of THF-H_2O-Solids Mixture

Solvent with dissolved polymer gives a higher index of refraction than would be expected for a given THF composition. Water composition can be found by the standard Karl Fischer determination. Solids content is found by percent weight loss on drying a 2-gram sample at 110° C. for 1/2 hour.

15. Analysis for Tetrahydrofuran Hydroperoxide

a. Reagents

1:4 conc. sulfuric acid-water mixture.
Potassium iodide, 10% solution.
Sodium thiosulfate, 0.02N solution.
Ammonium molybdate, 5% solution.

b. Procedure

1) Place 100 ml. distilled water in each of the two iodine flasks.
2) To each flask add 25 ml. of the 1:4 sulfuric acid-water mixture, 25 ml. of 10% potassium iodide, and a few drops of 5% ammonium molybdate solution.
3) Using a pipette, add 25 ml. of THF to one flask, stopper the flask, shake it, and place it in the dark for 15-20 minutes.
4) Titrate the contents of each flask with 0.02N sodium thiosulfate until the solution becomes colorless.

c. Calculation

% THF-peroxide = (ml. thio in sample - ml. thio in blank) (N of thio) (0.23)

16. Vinyl Chloride Composition in Reactor Overhead

Method - GLC

Column: length - 16 ft.
diameter - 1/4" stainless steel
packing - 33% dimethyl sulfolane on 45-60 mesh Chromosorb
Temperature - 25-30° C.
helium flow - 50 ml./min.

Detector Block - Glow-Mac Thermistor

ENGINEERING DATA

The exothermic heat of reaction in forming 1 lb. of ethylene/vinyl chloride/acrylamide solid was calculated to be 980 BTU/lb. This was determined by measuring the inlet and outlet temperatures as well as the weight of the cooling water supplied to the constant temperature reactor during a run. The cooling demand was found to be constant as a function of vinyl chloride uptake as shown in Figure 13. This cooling demand as a function of time is shown in Figure 12 and corresponds to the SFS addition program outlined in Figure 14.

The reaction speeds up when the acrylamide is added and the cooling demand increased to a maximum rate of 1100 BTU/hr. in the one gallon clave using the SFS curve shown in Figure 14.

Using a reactor temperature of 32° C., the heat transfer coefficient appears to remain a fairly constant 30-40 BTU/hr. ft.^{2} °F. over the entire run.

Figure 15 shows the cooling water temperature difference and weight as a function of time during the run.

TOXICITY AND HAZARDS

A. Vinyl Chloride

Vinyl chloride is a flammable liquid and a dangerous fire hazard. Its vapors form flammable mixtures with air at all temperatures down to 20° F. The limits of inflammability are 4-22% by volume in air. 10% vinyl chloride is dangerous to life of animals in from 30-60 minutes exposure, whereas 5% causes symptoms in less than an hour. Vinyl chloride is stored in a cool, ventilated area away from open flame, acute fire hazards, or powerful oxidizing agents. Personnel exposed to it should heed the warning of dizziness and disorientation, and remove themselves at once from air contaminated with it.[4]

B. Ethylene

No appreciable reaction occurs in ethylene at 2000 atmospheres below 100° C. and in ethylene at 250° C. below about 500 atmospheres. Nevertheless, even under these conditions, an uncontrollable reaction will propagate if by some mischance it is initiated. Ethylene is only safe from such propagations inside limiting conditions of which the following are examples:

Pressure	1000 atm.	400 atm.	200 atm.
Temperature	20° C.	100° C.	210° C.

The flammability limits of ethylene with oxygen are 2.9-27.9% by volume and with air are 2.75-28.6% by volume.[5]

C. Potassium Persulfate

Potassium persulfate is a strong oxidizing agent. Avoid contact of it with readily combustible materials.

D. Acrylamide Monomer

Acrylamide monomer is quite toxic, capable of causing nervous system disorders. Repeated small doses can prove to be toxic. Care must be taken to avoid repeated exposure by ingestion, inhalation or skin contact with the monomer or its aqueous solution.

E. Tetrahydrofuran

Tetrahydrofuran is a volatile, flammable liquid with a boiling point of 66° C. (151° F.). The flash point is -14.5° C. (6° F.) and its ignition temperature is 321° C. (610° F.). Upper and lower explosive limits in air are 11.8% and 2.0% by volume respectively.

Over exposure to the etherlike odor of tetrahydrofuran causes nausea, dizziness, headache and general ill feeling. Symptoms of over exposure to the vapor disappear quickly on access to fresh air. Contact of the skin with liquid tetrahydrofuran should be avoided since the solvent action will extract natural oils.

The dangers of peroxide build up in stored tetrahydrofuran are discussed in Section G, Part 5 of Discussion of Important Variables.

F. Reactor Vent Down

Care must be taken to adequately ground the blown down vessel and/or the vented latex relative to the high pressure reactor to avoid static discharge and a consequent monomer flash, especially when blowing into glass or polyethylene.

POLLUTION CONTROL

The off-gas from the reaction is flared to eliminate atmospheric pollution and an explosion hazard. Because of the relatively high density of vinyl chloride gas, high concentrations can accumulate near an atmospheric vent without a flare.

Large quantities of latex should not be sewered since solvents, acids, or bases subsequently added to the sewer will coagulate the latex and plug up sewer lines. Any latex that is sewered should be flushed with copious amounts of water.

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M. E. Gibbs

S. M. Balaban

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File Copy Approved by
Manager of Research:

E P Benzing (per J Q. 9)
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