



DOW CHEMICAL U.S.A.

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REACTIVE CHEMICALS COMMITTEE REVIEW - METHYL, 3-METHOXY PROPIONATE

Attached is a review packet prepared by Jimmy Mack, Sam Washington, and David Hunt for the upcoming Reactive Chemicals review on Production/Distillation of Methyl, 3-Methoxy Propionate.

Please review this before the meeting which will be held in the library conference room on October 16, 1986 at 12:15.

Gerald Wagener, Chairman
LA. AS&TL REACTIVE CHEMICALS COMMITTEE

attachment

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REACTIVE CHEMICALS REVIEW
FOR METHYL, 3-METHOXY PROPIONATE PRODUCTION
IN LAS&TL MINIPLANT

JIMMY MACK
SAM WASHINGTON
DAVID HUNT

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PROCESS DESCRIPTION

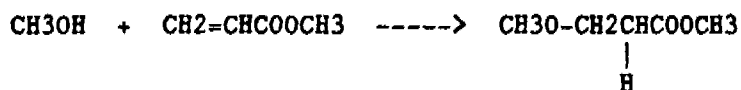
JHM 10/6/86

PURPOSE

The purpose of this project is to produce 25 gallons of methyl 3-methoxy propionate to sample potential customers in the paint and coating markets. An additional goal is to verify the technical and economic feasibility of a larger scale effort in which market development or commercial quantities may be made.

CHEMICAL REACTIONS

The reaction conditions will be at ambient temperature (25 C) up to 35 C and the pressures from atmospheric to 50 psig. The reaction uses 2 mole percent sodium methoxide as a catalyst and goes as follows:



METHANOL METHYL ACRYLATE MMP

There are no side reactions at the temperatures of operation and the only other known reaction in this system is the polymerization of the methyl acrylate. The heat of reaction to MMP has been estimated by Dave Firrup of the Michigan labs to be -2.6 kcal/mole of methyl acrylate. The heat of reaction as reported from the literature is -18.81 kcal/mole methyl acrylate.

PROCESS EQUIPMENT

The process will follow the basic flow sheet included on page 3. The reactor is a 26 gallon, medium pressure, 316 stainless steel unit previously used for the distillation of recycle toluene from the Triblocks Market Development Plant. It is rated at 220 psig at 375 F (191 C) and is equipped with a single speed turbine type agitator. A steam and water jacket provides temperature control. Auxillary equipment on the reactor includes a 4 inch stainless steel packed column, reflux condenser, total condenser, and 20 gallon receiver pot. The methyl acrylate will be handled in two 7.5 gallon LPG tanks equipped with dip and vent pipes. These will be placed on a digital scale and the contents pumped using a diaphragm metering pump through a control valve to the reaction vessel. All of these units are protected by pressure relief devices and are on the pressure vessel program. The reactor and distillation column is handled by a PDP-11 computer.

PROCEDURES

The reactor, column, receiver, and interconnecting piping will be cleaned and dried. The methyl acrylate cylinders will be filled in a lab hood from 5 gallon cans. The filled cylinders will be padded to 100 psig with a dry gas mixture of 6% oxygen and the balance being nitrogen. The sodium methoxide will be weighed out and loaded by vacuum into the reactor which has been nitrogen purged. The methanol will

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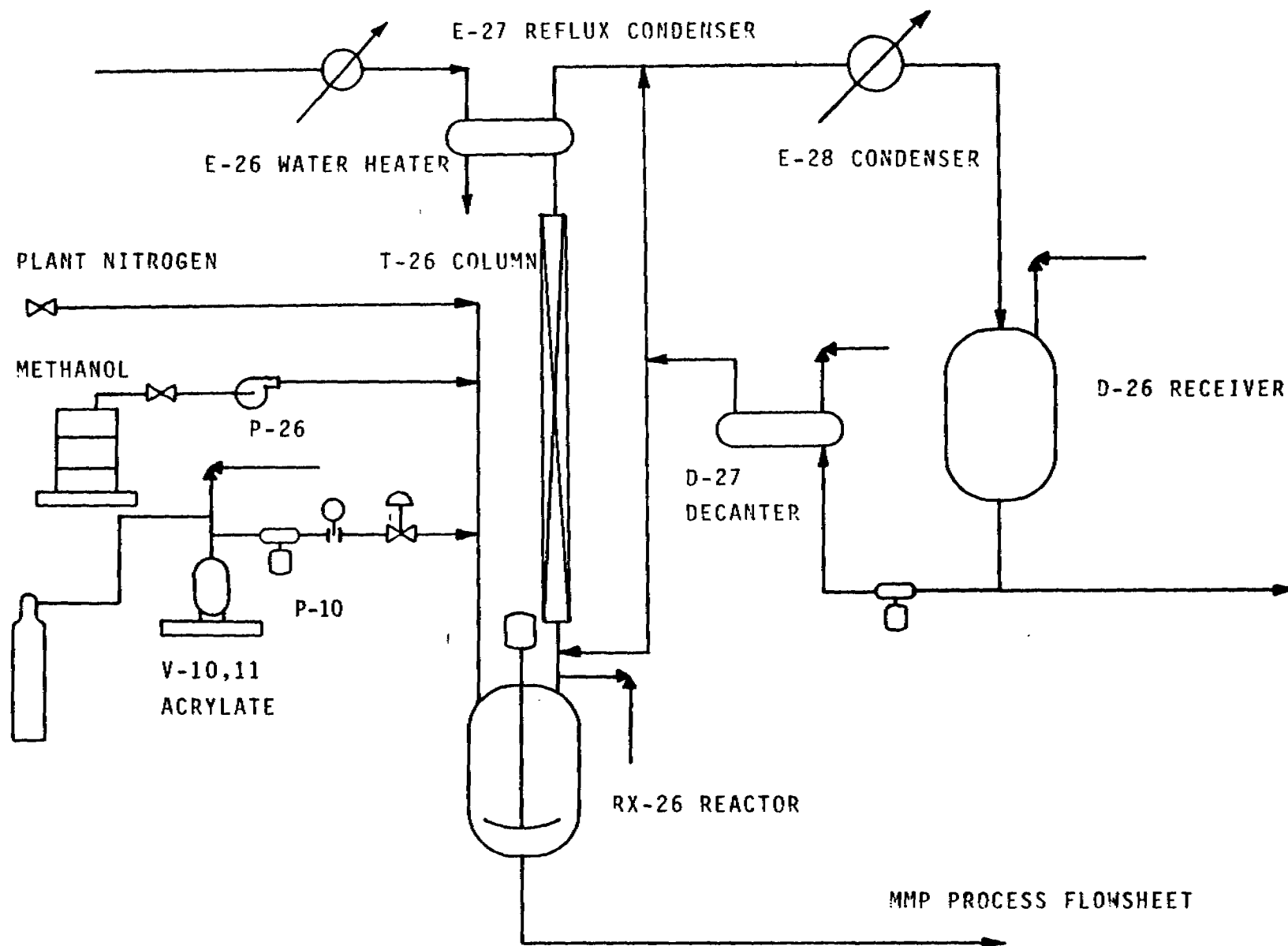
then be batch loaded from the drum scale using residual vacuum and the loading pump. The agitator will be started and the catalyst allowed to mix for 1/2 hour.

With full cooling water flowing on the jacket of the reactor, the methyl acrylate will be metered into the reaction mixture at a rate controlled to maintain the temperature below 35 C and to limit the amount of unreacted acrylate to 0.5-1.0% of the total by GC analysis. This amount should allow us to keep the reactor isothermal even if all of the unreacted acrylate polymerizes. The addition will continue until all of the methyl acrylate in the two cylinders is exhausted. The reaction will be allowed to post react until the residual acrylate is less than 1%. An equal molar charge of acetic acid will be added from a sample cylinder to neutralize the sodium methoxide. This will be allowed to react for 2 hours.

The resultant mix of methanol, methyl acrylate, and MMP will then be distilled to separate essentially pure MMP. The methanol and residual methyl acrylate will be taken over in a lights cut at atmospheric pressure, and then the MMP will be distilled over under vacuum. The bottoms of the still which will contain acetic acid, sodium acetate, and MMP will be dumped and burned as waste.

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REACTIVE CHEMICALS DATA

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LIBRARY LISTS: 17 DTA, FP, AND ARC DONE TO DATE

OF PARTICULAR INTEREST:

RCM 82-874: ARC FOR FLAMMABILITY LIMITS IN O₂-N₂ ATMOSPHERE

RCT 83-195: DTA OF METHYL ACRYLATE

RCM 86-967: HEAT OF REACTION ESTIMATION

RCL 86-204A: DTA OF METHYL ACRYLATE, METHANOL, AND
SODIUM METHOXIDE

RCL 86-204B: DTA OF METHYL ACRYLATE

RCL 86-204C: DTA OF METHYL ACRYLATE AND METHANOL

KNOWN REACTIVE CHEMICAL HAZARDS:

EXOTHERMIC POLYMERIZATION OF METHYL ACRYLATE AS LOW AS 37 TO 40 C
HEAT OF REACTION: -18.81 KCAL/MOLE

METHYL ACRYLATE INHIBITED FOR THIS WITH A COMPOUND SENSITIVE TO
LACK OF OXYGEN AND MOISTURE

SLIGHT EXOTHERMIC REACTION OF METHANOL AND METHYL ACRYLATE IN THE
PRESENCE OF SODIUM METHOXIDE
HEAT OF REACTION: -2.6 KCAL/MOLE (ESTIMATE TO +/- 3 KCAL/MOLE)

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POTENTIAL CHEMICAL HAZARDS

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CHEMICAL

HAZARDS

METHANOL

FLAMMABLE--FP: 60.8 F
FL: 6.0-36.5%

TOX--SKIN, EYE, INHALATION
INGESTION

METHYL ACRYLATE

FLAMMABLE--FP: -8.3-2.8 C
FL: 2.8-25%

TOX--EYE, SKIN, INHALATION
INGESTION (SEVERE)

SODIUM METHOXIDE

FLAMMABLE--FP: 60.8 F
FL: 6.0-36.5%

TOX--EYE, SKIN, INHALATION
INGESTION (STRONG BASE)

ACETIC ACID

FLAMMABLE--FP: 104 F
FL: 4-16%

TOX--EYE, SKIN, INHALATION
INGESTION (STRONG ACID)

MMP

FLAMMABLE--FP: 108 F
FL: NOT DETERMINED

TOX--PRELIMINARY ACUTE ON INHALATION
AND INGESTION INDICATES MODERATE
TOXICITY

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PROTECTIVE EQUIPMENT REQUIRED

CHEMICAL

METHANOL	RUBBER GLOVES, MONOGOGGLES
METHYL ACRYLATE	RUBBER GLOVES, MONOGOGGLES, SAMPLING RESPIRATOR (HANDLE IN LAB HOOD)
SODIUM METHOXIDE	RUBBER GLOVES, MONOGOGGLES
ACETIC ACID	RUBBER GLOVES, MONOGOGGLES
CRUDE MMP REACTOR SAMPLES	RUBBER GLOVES, MONOGOGGLES, SAMPLING RESPIRATOR
LIGHTS CUT SAMPLES	RUBBER GLOVES, MONOGOGGLES, SAMPLING RESPIRATOR
FINISHED MMP	RUBBER GLOVES, MONOGOGGLES, SAMPLING RESPIRATOR
BOTTOMS OF STILL	RUBBER GLOVES, MONOGOGGLES, SAMPLING RESPIRATOR

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PROCESS ALARMS

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REACTOR

CURRENT LIMIT

HIGH PRESSURE	100 PSIG *
HIGH TEMPERATURE	37 C *
AGITATOR SHUTDOWN	0 RPM *
HIGH REACTOR LEVEL	80 % *
LOW REACTOR LEVEL	20 %
LOW CYLINDER WEIGHT	37 LB
HIGH PUMP DISCHARGE TEMPERATURE	35 C *

DISTILLATION COLUMN

HIGH CONDENSER TEMPERATURE	30 C
HIGH RECEIVER TANK LEVEL	80 %
LOW RECEIVER TANK LEVEL	80 %

* THESE ARE TIED INTO A SHUT DOWN SEQUENCE THAT STOPS THE FEED AND PUTS THE REACTOR AND DISTILLATION SYSTEM ON FULL COOLING

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GENERALIZED PROCEDURES

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REACTION

CLEAN AND DRY THE REACTOR AND DISTILLATION SYSTEMS

LOAD SODIUM METHOXIDE

LOAD THE METHANOL

AGITATE THE SOLUTION FOR 1/2 HOUR AT AMBIENT TEMPERATURE

PUMP THE METHYL ACRYLATE INTO THE REACTOR AT A RATE TO KEEP THE TEMPERATURE BELOW 35 C AND THE UNREACTED METHYL ACRYLATE BELOW 0.5-1.0 %

POST REACT THE METHYL ACRYLATE UNTIL THE RESIDUAL IS LESS THAN 1%

LOAD THE ACETIC ACID TO NEUTRALIZE THE SODIUM METHOXIDE

REACT THE MIXTURE FOR 2 HOURS

DISTILLATION

HEAT UP THE COLUMN UNDER TOTAL REFLUX

SLOWLY STRIP OFF THE METHANOL AND METHYL ACRYLATE

DRAIN THE RECEIVER TANK

COOL THE SYSTEM DOWN AND ADD MORE METHANOL

STRIP OFF THE EXTRA METHANOL TO WASH THE LINES

DRAIN THE RECEIVER TANK

PUT THE COLUMN UNDER VACUUM AND STRIP OFF THE MMP

DRAIN THE RECEIVER TANK AND STILL POT

FILLING THE ACRYLATE CYLINDERS

CLEAN AND DRY THE CYLINDERS

FILL THEM IN THE LAB HOOD

CONNECT THEM TO THE CYLINDER STATION AND PAD WITH PAD GAS

DISCONNECT AND DEPAD IN THE LAB HOOD

FILLING THE ACID SAMPLE CYLINDER

CLEAN AND DRY THE CYLINDER

FILL IT WITH A WEIGHED AMOUNT IN THE LAB

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CONNECT TO THE PROCESS TIE POINT
PAD INTO THE REACTOR USING NITROGEN
DISCONNECT AND DRAIN IN LAB

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