



Granular Detergents Manufacture- Generic Scenario for Estimating Occupational Exposures Environmental Releases -Draft

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March 1991

GRANULAR DETERGENTS MANUFACTURE

USUALLY, THE PMN IS AN INGREDIENT USED IN SYNTHETIC DETERGENTS FORMULATION.

THERE IS NEITHER A SINGLE PROCESS IN THE MANUFACTURE OF DETERGENTS NOR A UNIFORM FORMULA OR RECIPE IN TERMS OF THE KINDS AND QUANTITIES OF INGREDIENTS. THE ASSUMPTIONS USED IN THIS SCENARIO, THEREFORE, SHOULD BE USED ONLY WHEN THE REQUIRED DATA ARE NOT AVAILABLE.

* THERE ARE SEVERAL HUNDRED MANUFACTURING SITES.

* BASIC INGREDIENTS

ASSUME: 25% SURFACTANT (10-40), 40% BUILDER (25-50), 5% CORROSION INHIBITOR (3-8), <1% ANTIREDEPOSITION AGENT, <0.1% FLOURESCENT WHITENING AGENT, <0.1% COLORANTS, <0.5% PERFUMES OR FRAGRANCES, <0.1% ENZYMES, OXYGEN BLEACH AND SUDS CONTROL AGENT.

IT SHOULD ALSO BE NOTED THAT SURFACTANT, USUALLY A PASTE, IS A PRODUCT OF AN ORGANIC INTERMEDIATE (LINEAR ALKYLATE, FATTY ALCOHOLS, OR ALKYL ETHER) AND A SULFATING OR SULFONATING AGENT.

* TERMINOLOGIES AND DETAILED PROCESS DESCRIPTION ARE PRESENTED IN ATTACHMENT 1.

* PROCESS FLOW DIAGRAMS ARE INCLUDED IN ATTACHMENT 2.

* DETAILED INFORMATION ON ENVIRONMENTAL RELEASES IS PRESENTED IN ATTACHMENT 3.

CEB WORK SHEETS
GRANULAR DETERGENTS MANUFACTURE

PMN #:
DATE COMPLETED:
BY:

- * TOTAL MASS OF PMN OR TMPMN (GIVEN): = _____ KG
- * % PMN PURITY (GIVEN) = _____ %
- * % PMN IN DETERGENT (GIVEN OR ASSUMED): = _____ %
- * PROCESS DESCRIPTION
RAW MATERIAL RECEIPT AND STORAGE ----> PASTE MAKING
(SURFACTANT) -----> ADDING ADDITIVES -----> MIXING AND
PUMPING ----> SPRAY DRYING ----> COOLING, SCREENING, AND
MIXING ----> PACKAGING.
- * NUMBER OF SITES OR NS (GIVEN OR CALCULATED) = _____ SITES
 - * IF NS IS GIVEN: USE METHOD 1 TO ESTIMATE # DAYS
OPERATION IF # DAYS IS NOT GIVEN
 - * IF NOT GIVEN: USE METHOD 2 TO ESTIMATE # DAYS OPERATION
THEN CALCULATE NS
- * DAYS OF OPERATION OR DOP (GIVEN OR CALCULATED) = _____ DAYS
ASSUMPTIONS: 300,000 KG DETERGENT/SITE/DAY (500,000 MAX)
24 HR/DAY OPERATION, 3 SHIFTS/DAY

METHOD 1: IF NUMBER OF SITES IS GIVEN

PMNPSPY = TMPMN / NS = _____ KG/SITE/YR
DOP = PMNPSPY / (300,000 * %PMN IN DETERGENT)
= _____ DAYS/SITE/YR
IF DOP > 300 DAYS/YR, THEN DOP = 300 AND
PMNPSPD (KG PMN/SITE/DAY) = PMNPSPY/DOP
PMNPSPD = _____ KG PMN/SITE/DAY
IF PMNPSPD > (500,000 * %PMN IN DETERGENT), CALL
SUBMITTER SINCE # SITES SHOULD BE HIGHER

METHOD 2: IF NUMBER OF SITES IS NOT GIVEN

ASSUME: DOP = 300 DAYS/SITE/YR
PMNPSPD = (300,000 * %PMN IN DET) = _____ KG/SITE/DAY
PMNPSPY = 300 * PMNPSPD = _____ KG/SITE/YR
NS = TMPMN / PMNPSPY = _____ SITES

COMMENTS: _____

OCCUPATIONAL EXPOSURE

* NUMBER OF WORKERS:

- (GIVEN) OR ASSUME 3 (1/SHIFT) **MATERIAL HANDLERS** INVOLVED IN HANDLING OF INGREDIENTS
- (GIVEN) OR 3 (1/SHIFT) **WET-END OPERATORS** RESPONSIBLE FOR MIXING AND PUMPING OPERATION
- (GIVEN) OR 3 (1/SHIFT) **DRY-END OPERATORS** RESPONSIBLE FOR DRYING AND SCREENING OPERATION
- (GIVEN) OR 6-9 (2-3/SHIFT) **PACKERS** RESPONSIBLE FOR PACKAGING OPERATION
- (GIVEN) OR 3-6 **MAINTENANCE WORKERS** INVOLVED IN CLEANING OF EQUIPMENT

NOTE: PERFUME, OXYGEN BLEACH AND ENZYMES ARE SOMETIMES ADDED AFTER THE SCREENING OPERATION AND THEREFORE, THE TOTAL NUMBER OF WORKERS EXPOSED IN THESE CASES MAY BE LESS BY 6 WORKERS (3 WET-END AND 3 DRY-END OPERATORS).

TOTAL NUMBER OF WORKERS EXPOSED = _____

NUMBER OF DAYS EXPOSED OR NDE = DOP OR 250 MAX. = _____ **DAYS**

MATERIAL HANDLERS: NDE = _____ **DAYS**

FOR SOLID PMN (DUST EXPOSURE FROM HANDLING OF BAGS):

INHALATION = $150 * (\%PMN \text{ PURITY}) =$ _____ **MG/DAY**

DERMAL = $(6500-18200) * (\%PMN \text{ PURITY}) =$ _____ **MG/DAY**
(THIS IS WORST CASE. HOWEVER, A LOT OF TIMES, EQUIPMENT IS USED TO DUMP BAGS AND THEREFORE, DERMAL EXPOSURE WOULD BE UNLIKELY)

FOR LIQUID PMN (EXPOSURE FROM CONNECTING FEED HOSE, ASSUME 1 INCH. OPENING)

INHALATION = NEGLIGIBLE IF V.P. IS LOW OR

WORST:

$$C_v = 0.628 * P * (1/29 + 1/M)^{.25} * 5 / (MW^{.165} * 2.54^{0.5})$$

= _____ **PPM**

$$\text{THEN } C_m = C_v * MW / 24.45 = \text{_____ } \text{MG/M}^3$$

TYPICAL:

$$Cv = (\text{WORST CASE } Cv) / 30 = \text{_____ PPM}$$

$$\text{THEN } Cm = Cv * MW / 24.45 = \text{_____ MG/M}^3$$

$$\text{EXPOSURE} = Cm * 1.25 * (1 \text{ HR EXPOSED}) * (\%PMN \text{ PURITY})$$

$$\text{WORST} = \text{_____ MG/DAY} \quad \text{TYPICAL} = \text{_____ MG/DAY}$$

$$\text{DERMAL} = (1300-3900) * (\%PMN \text{ PURITY}) = \text{_____ MG/DAY}$$

WET-END OPERATORS (SAMPLING OF MIXTURE) NDE = _____ DAYS

INHALATION = NEGLIGIBLE IF V.P IS LOW OR

WORST:

$$Cv = 16 * P * (1/29 + 1/MW)^{.25} / MW^{.165} = \text{_____ PPM}$$

$$\text{THEN } Cm = Cv * MW / 24.45 = \text{_____ MG/M}^3$$

TYPICAL:

$$Cv = (\text{WORST CASE } Cv) / 53.33 = \text{_____ PPM}$$

$$\text{THEN } Cm = Cv * MW / 24.45 = \text{_____ MG/M}^3$$

$$\text{EXPOSURE (MG/DAY)} = Cm * 1.25 * (1 \text{ HR EXPOSED}) * (\%PMN \text{ IN DETER})$$

$$\text{WORST} = \text{_____ MG/DAY} \quad \text{TYPICAL} = \text{_____ MG/DAY}$$

$$\text{DERMAL} = (650-1950) * (\%PMN \text{ IN DETER}) = \text{_____ MG/DAY}$$

DRY-END OPERATORS (EXPOSURE TO PARTICULATES ONLY) NDE = _____ DAYS

INHALATION = (150) * (%PMN IN DETERGENT) = _____ MG/DAY
(EXPOSURE TO DUST FROM EQUIPMENT LEAKS AND POSSIBLY
FROM HANDLING OF FINES FROM DUST COLLECTOR/CYCLONE AS
WELL AS CLEANING OF THE SPRAY-DRYER EVERY 3 DAYS)

DERMAL EXPOSURE

TYPICAL = NOT LIKELY

$$\text{WORST} = (6500-18200) * (\%PMN \text{ IN DETER}) = \text{_____ MG/DAY}$$

(WORST CASE EXPOSURE MAY OCCUR ONCE A DAY FROM
DUMPING OF FINES BACK INTO SYSTEM. HOWEVER, IT
IS EXPECTED THAT MANY PLANTS WOULD HAVE A RECYCLE
STREAM AND THEREFORE, THERE WOULD BE NO EXPOSURE)

PACKERS (EXPOSURE TO PARTICULATES) NDE = ____ DAYS

INHALATION = (150) * (%PMN IN DETERG) = ____ MG/DAY
(WORST CASE. HOWEVER, EXPOSURE SHOULD BE MUCH LESS
SINCE THERE IS LOCAL VENTILATION SYSTEM.

DERMAL = (1300-3900) * (%PMN IN DETER) = ____ MG/DAY

MAINTENANCE WORKERS (EXPOSURE TO PARTICULATES)

NDE = DOP/3 = ____ DAYS

INHALATION = SAME AS FOR PACKERS = ____ MG/DAY

DERMAL = SAME AS FOR PACKERS = ____ MG/DAY

ENVIRONMENTAL RELEASES

AQUEOUS WASTE:

ASSUME 1% FROM EQUIPMENT CLEANING AND 0.5% FROM SPILLAGE.

RELEASE = (.005 - .015) * PMNPSD = ____ KG/SITE/DAY

-----> TO MUNICIPAL WASTE TREATMENT SYSTEM

(UP TO 1% OR ____ KG/SITE/DAY COULD BE RECYCLED)

AIR:

NEGLIGIBLE.

INCINERATION:

NONE.

SOLIDS:

ASSUME 1% FROM EQUIPMENT CLEANING AND 1% FROM SPILLAGE

RELEASE = (.01 - .02) * TMPMN = ____ KG/YR

-----> DISPOSED OF AS A SOLID WASTE (LANDFILL)

(UP TO 1% OR ____ KG/YR COULD BE RECYCLED)

COMMENTS: _____

ATTACHMENT 1

TERMINOLOGIES AND PROCESS DESCRIPTION

- * SURFACTANTS: ORGANIC COMPOUNDS, A PORTION OF WHICH IS HYDROPHILIC AND A PORTION OF WHICH IS HYDROPHOBIC BUT HAS AN AFFINITY FOR SOIL. THEIR ROLE INCLUDES REDUCING THE SURFACE TENSION OF THE WATER TO INCREASE PENETRATION IN CLOTHES AND SOIL AND SEQUESTING THE SOIL ONCE IT IS SEPARATED FROM THE FABRIC. THERE ARE THREE BASIC KINDS: ANIONIC, CATIONIC, AND NONIONIC. SOME COMMON SURFACTANTS: LINEAR ALKYL BENZENE SULFONATE (LAS), ALKYL ETHOXY SULFATE, AND ALKY ETHOXYLATES. SURFACTANT (PASTE FORM) IS THE PRODUCT OF AN ORGANIC INTERMEDIATE (I.E. LINEAR ALKYL BENZENE) AND A SULFONATING AGENT (I.E. MIXTURE OF SULFURIC ACID AND SULFUR TRIOXIDE). USUALLY HIGHLY VISCOUS LIQUIDS.
- * BUILDERS: WHEREAS SURFACTANTS EXERT THEIR HEAVIEST IMPACT ON ORGANIC SOIL, BUILDERS IMPACT ON INORGANIC SOIL AS WELL AS REDUCE THE HARDNESS OF THE WATER EITHER BY SEQUESTING OR PRECIPITATING WATER HARDNESS IONS. EXAMPLES OF COMMONLY USED BUILDERS INCLUDE SODIUM PHOSPHATES, CITRATES, SILICATES, CARBONATES, AND ALUMINO SILICATES.
- * CORROSION INHIBITORS: PROTECTS THE WASING MACHINE PARTS FROM CORROSION. SODIUM SILICATE IS COMMONLY USED. PHYSICAL FORM RANGES FROM A VISCOUS SOLUTION TO A DUSTY, DRY MATERIAL IN BAGS.
- * ANTIREPOSITION AGENTS: PREVENTS SOIL FROM REDEPOSITING ON FABRICS ONCE IT IS REMOVED. SODIUM CARBOXYMETHYLCELLULOSE (CMC) IS COMMONLY USED. CMC IS A DRY MATERIAL NORMALLY HANDLED IN BAGS.
- * FLUORESCENT WHITENING AGENTS: COMPLEX ORGANIC MOLECULES CAPABLE OF ABSORBING ULTRAVIOLET LIGHT AND EMITTING VISIBLE LIGHT TO ENHANCE FABRIC WHITENESS OR BRIGHTNESS. THEY ARE USED IN VERY SMALL QUANTITIES AND RECEIVED IN FIBER DRUMS, AND SPECIFIC BATCH AMOUNTS CAN BE PREWEIGHED OR SCOOPED DIRECTLY FROM THE DRUM INTO A SLURRY TANK AND THEN INTO THE CRUTCHER.
- * COLORANTS: THESE PROVIDE ANESTHETIC SUPPORT FOR THE PRODUCT AND FABRIC.

THE ABOVE MATERIALS ARE FED INTO THE CRUTCHER, WHICH IS THE PRIMARY MIXER, WATER IS ADDED, AND THOROUGH MIXING IS ACCOMPLISHED. THIS PROCESS CAN GENERATE NOISE AND HEAT, WHICH WOULD REQUIRE EVALUATION TO DETERMINE THE DEGREE OF HAZARD. ONCE MIXING IS ACCOMPLISHED, THE BATCH IS TRANSFERRED TO A "DROP TANK". FROM THE DROP TANK THE PASTELIKE MIXTURE IS PUMPED VIA A SERIES OF HIGH AND LOW PRESSURE PUMPS TO THE SPRAY-DRYING TOWER. AT THIS POINT, THE PROCESS CHANGES FROM ESSENTIALLY A BATCH-TYPE PROCESS TO A CONTINUOUS PROCESS.

ATTACHMENT 1 (CON'T)

TO PRODUCE GRANULES, THE DETERGENT MIX IS HEATED AND PIPED TO THE TOP OF A SEVEN-STORY SPRAY-DRYING TOWER. HERE THE MIX IS FORCED THROUGH FINE NOZZLES UNDER HIGH PRESSURE. WHEN IT COMES OUT, MOST OF THE WATER FLASHES OFF, LEAVING DRY GRANULES OF PRODUCT. THE GRANULES FALL IN A FINE SPRAY THROUGH HOT AIR RISING FROM THE BOTTOM OF THE TOWER. THE GRANULES ARE TAKEN FROM THE BOTTOM OF THE TOWER AND ENTER AN AIR LIFT. HERE LARGER GRANULES ARE SCREENED OUT AND SMALLER ONES ARE FILTERED OUT, LEAVING ONLY ONE SIZE. AT THIS POINT, PERFUME AND OTHER DRIED INGREDIENTS ARE ADDED TO MAKE THE FINISHED PRODUCT.

ONCE THE PASTE IS TRANSFORMED INTO A GRANULAR PRODUCT AT THE BASE OF THE TOWER, DUST AND SPILLAGE CONTROL BECOME AN IMPORTANT PROCESS AND HYGIENE CONSIDERATION.

ENVIRONMENTAL CONTROL IS AN INTEGRAL PART OF THE SPRAY-DRYING OPERATION. EMISSIONS FROM THE TOWER ARE TREATED IN THE ENVIRONMENTAL CONTROL EQUIPMENT (COLLECTOR, SCRUBBERS, PRECIPITATORS), WHICH LEAVES ONLY HOT WATER VAPORS TO ESCAPE THROUGH THE STACK.

* PERFUMES: USUALLY SPRAYED INTO THE STREAM OF GRANULES AS A LIQUID.

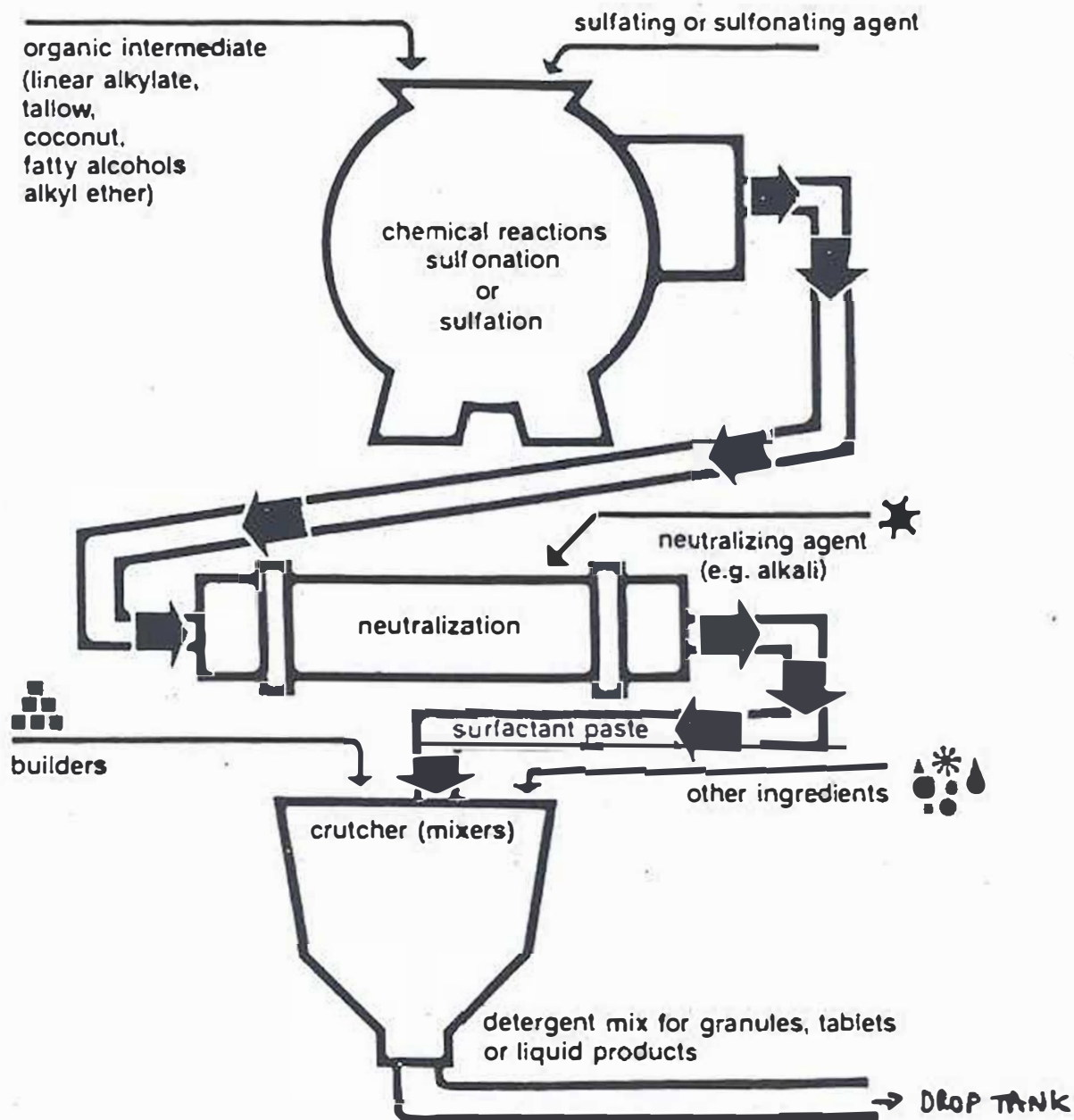
* OXYGEN BLEACH: USUALLY THIS IS SODIUM PERBORATE, WHICH IS MANUALLY INTRODUCED BY DUMPING BAGS. IT CAN BE DUSTY.

* ENZYMES: THESE ARE USED INFREQUENTLY. THEY ARE NORMALLY RECEIVED FROM SUPPLIERS IN FIBER DRUMS OR "BIG BAGS" AS EITHER ENCAPSULATES OR SOME FORM OF DUST SUPPRESSED PARTICULATE AND ADMIXED INTO THE FLOW OF GRANULES.

ATTACHMENT 2 - FLOW DIAGRAM 1

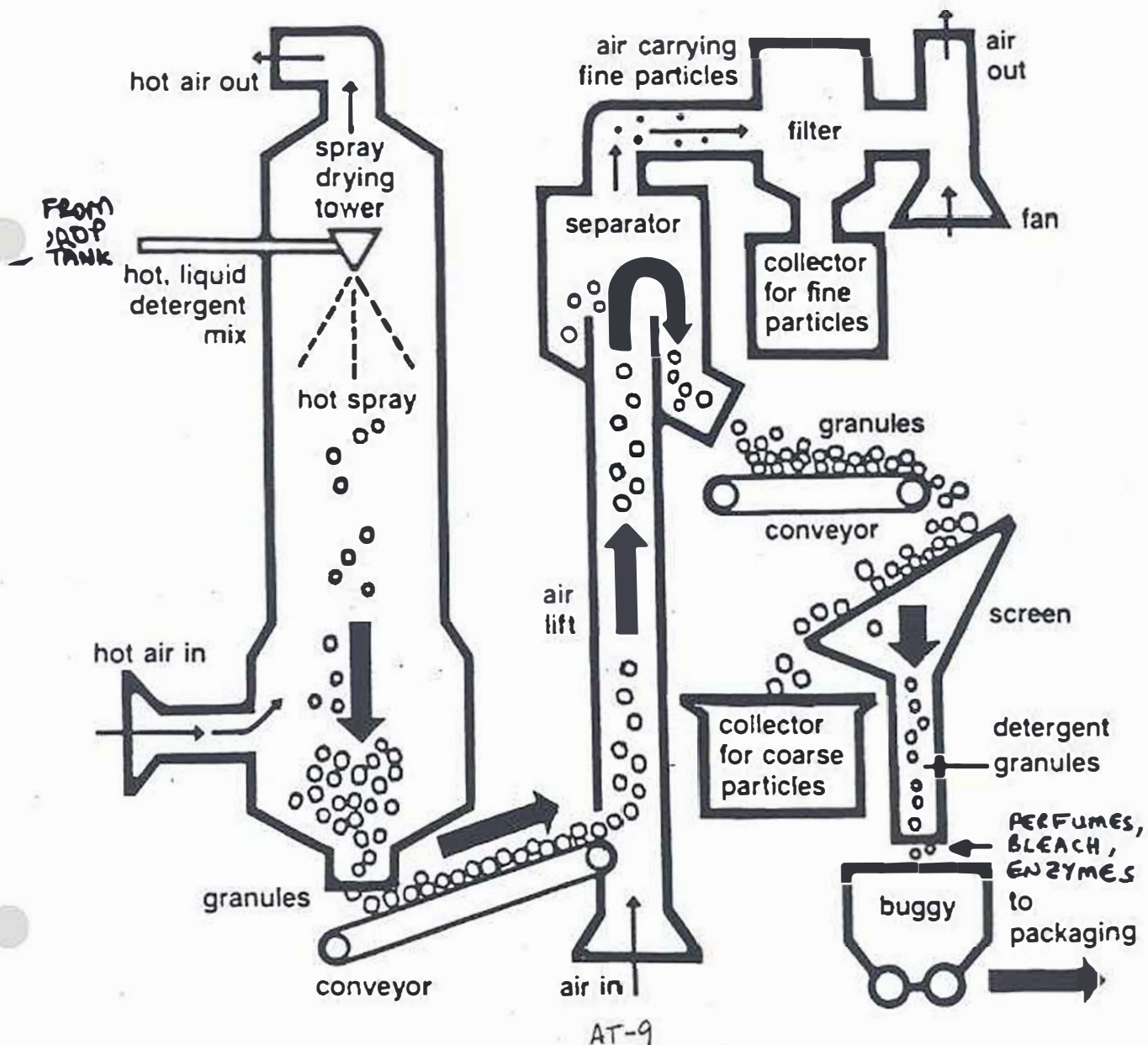
SYNTHETIC DETERGENT PASTE MAKING

The top section of the diagram shows how the surface active agent is produced. This is then neutralized and mixed with builders and other ingredients in the large tank (crutcher) shown at the bottom.



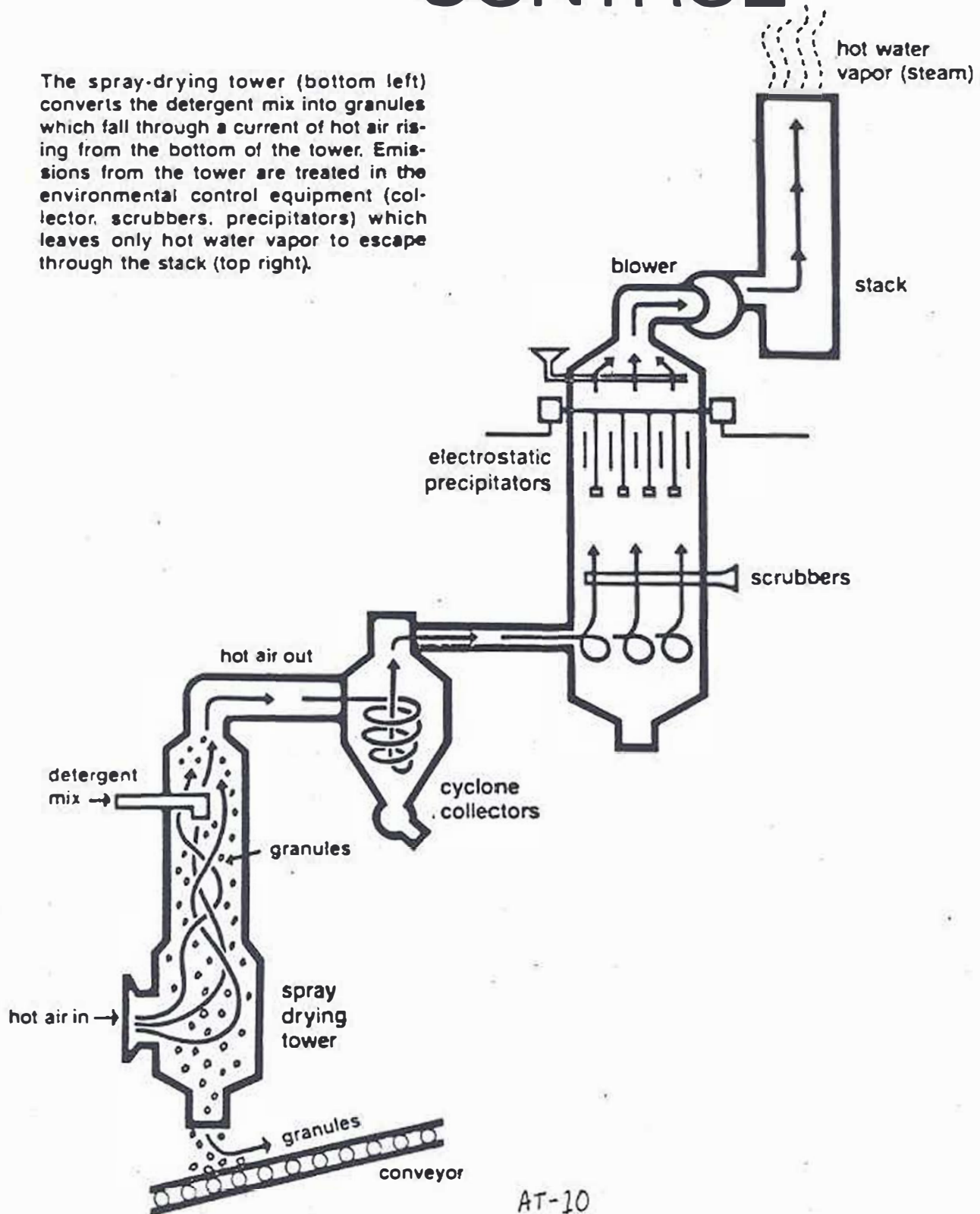
MAKING DETERGENT GRANULES

Most heavy-duty laundry detergents come in granular (powder) form. To produce granules, the detergent mix is heated and piped to the top of a seven story spray-drying tower. Here the mix is forced through fine nozzles under high pressure. When it comes out, most of the water flashes off, leaving dry granules of product. These granules fall in a line spray through hot air rising from the bottom of the tower. The granules are taken from the bottom of the tower and enter an air lift. Here larger granules are screened out and smaller ones are filtered out leaving only one size. At this point, perfume and other dried ingredients are added to make the finished product.



ENVIRONMENTAL CONTROL

The spray-drying tower (bottom left) converts the detergent mix into granules which fall through a current of hot air rising from the bottom of the tower. Emissions from the tower are treated in the environmental control equipment (collector, scrubbers, precipitators) which leaves only hot water vapor to escape through the stack (top right).



ATTACHMENT 3

ENVIRONMENTAL RELEASES

AQUEOUS WASTE:

AQUEOUS RELEASE A: FROM EQUIPMENT

DUE TO PRODUCT CHANGE AND BUILDUP OF COMBUSTIBLE DEPOSITS, THE SPRAY TOWERS ARE PERIODICALLY SHUT DOWN AND CLEANED. THIS PRACTICE VARIES FROM TWO OR THREE TIMES A WEEK TO ONCE IN TWO WEEKS OR LONGER. ONE THING THAT ALL TOWER OPERATIONS SHARE IS THE CLEANING PROCESS. FIRST, THE EASILY AVAILABLE MATERIAL STICKING TO THE TOWER WALLS IS SCRAPPED TO BE RECYCLED IF AT ALL POSSIBLE, OR SENT TO SOLID WASTE.

MEN ARE SENT INTO THE TOWER WITH ABRADING EQUIPMENT TO CONTINUE THE DRY CLEANING PROCESS. HERE AGAIN, THE PRODUCT IS USUALLY PRESERVED FOR REUSE OR DISPOSED OF AS A SOLID WASTE.

ASSUME: SPRAY-DRYER AND CRUCHER ARE CLEANED ONCE EVERY THREE DAYS AND 1% OF THE DAILY PMN USED IS RELEASED WITH THE WATER.

AQUEOUS RELEASE A = $.01 * (\text{PMNPSPD}) = \underline{\hspace{2cm}}$ KG/SITE/DAY

THE AQUEOUS RELEASE A IS USUALLY RECYCLED TO MIXER OT IT COULD BE RELEASED TO MUNICIPAL WASTE TREATMENT SYSTEM.

AQUEOUS RELEASE B: FROM SPILLAGE

ASSUME 0.5% OF THE DAILY PMN USED IS DISSOLVED IN CLEAN-UP WATER WHICH IS USUALLY RECYCLED OR SENT TO MUNICIPAL WASTE TREATMENT SYSTEM.

AQUEOUS RELEASE B = $.005 * (\text{PMNPSPD}) = \underline{\hspace{2cm}}$ KG/SITE/DAY

THE AQUEOUS RELEASE B IS USUALLY SENT TO MUNICIPAL WASTE TREATMENT SYSTEM

TOTAL AQUEOUS RELEASE = $A + B = \underline{\hspace{2cm}}$ KG/SITE/DAY

AIR:

NEGLIGIBLE. THE AIR COMING FROM THE TOWER CARRIES DUST PARTICLES WHICH MUST ESSENTIALLY BE ELIMINATED BY THE DUST COLLECTION SYSTEM TO MEET AIR QUALITY STANDARDS. ALSO, THE BLOWER IS USUALLY LOCATED AT THE HIGHEST ELEVATION (ON THE ROOF OF THE MANUFACTURING BUILDING). SOME BLOWERS EVEN HAVE A STACK.

INCINERATION:

NONE.

ENVIRONMENTAL RELEASES (CON'T)

SOLID WASTE:

RELEASE A: FROM EQUIPMENT

ASSUME: SPRAY-DRYER AND CRUCHTER ARE CLEANED ONCE EVERY THREE DAYS AND 1% OF THE DAILY PMN USED STICKS TO THE WALLS OF THE VESSELS.

RELEASE A = .01 * (TMPMN) = _____ KG/YEAR

-----> RECYCLED OR DISPOSED OF AS A SOLID WASTE (LANDFILL)

RELEASE B: FROM SPILLAGE

ASSUME: 1% OF PMN USED

RELEASE B = .01 * (TMPMN) = _____ KG/YEAR

-----> DISPOSED OF AS A SOLID WASTE (LANDFILL)

TOTAL SOLIDS RELEASED = A + B = _____ KG/YEAR

REFERENCES

1. Shreve, Norris R. and Joseph A. Brink, Jr. Chemical Process Industries, fourth edition, McGraw-Hill, Chapter 29.
2. Industrial Hygiene Aspects of Plant Operations, volume 1, Chapter 57.
3. SRI. Aliphatic Surfactants, March 1974.
4. The Mitre Corporation. Technical Review for Pre-Manufacture Review of New Chemical Substances, September 1985.
5. Notes from 11/15/1988 Proctor and Gamble Plant Trip.
6. Some assumptions used were based on interpretation of flow diagrams and industry experience with solids handling equipment in similar processes.