OPERATING TECHNOLOGY MANUAL

SOLUTION VINYL RESINS PROCESS

BY

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UNION CARBIDE CORPORATION

TEXAS CITY, TEXAS

JANUARY, 1982

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TABLE OF CONTENTS

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INTRODUCTION

The Texas City Solution Vinyls Unit is by any standard a large and complicated production facility. So far as we know, for manufacturing vinyl resins it is the only process worldwide that utilizes a continuous reaction step and the only process where the resins are manufactured in solution. These two unique features have their advantages and disadvantages.

Considerable lag time is built into this continuous process, causing problems in controlling the physical properties of the produced resin. A change at the beginning of the process may not be noticeable in the final product until 24 hours later. Obviously, this is a disadvantage. However, "the other side of the coin" is that this "sluggishness" prevents erratic changes in certain properties, resulting in the production of a rather uniform product. So, the good news is that within a customer shipment the product will be quite uniform and from one shipment to the next the customer receives essentially the same quality material.

Resins manufactured by the solution process are generally low in molecular weight (by vinyl resin standards) and high in such monomers as vinyl acetate. This combination of properties causes the resins to be readily soluble in most organic solvents. Obviously, our solution process would not work if the resins were not soluble in organic solvents such as acetone and MEK. The ease with

which solution vinyl resins can be placed in solution is one of their major advantages. Most vinyl resins sold in the world today are made by the batch suspension process and are high in vinyl chloride content. These resins are insoluble in most organic solvents.

The precipitation of solution vinyl resins to obtain a dry powder is a specialized, complex process so while we have the advantage of producing a unique resin that is readily soluble we have the disadvantage of an expensive manufacturing process.

Another quality advantage of our resin is its freedom from suspending agents and other additives found in most vinyl resins. This exceptional purity is important when the resin is used in applications such as beverage can linings that bring it into contact with food products.

If the solution vinyl resins operation is to be carried out safely, economically, and with good productivity while producing resins of high quality, a multitude of important operating conditions must be adhered to along the way. This manual attempts to define what some of those conditions are.

GLOSSARY OF TERMS

AS RELATED TO THE SOLUTION VINYLS UNIT

1)	BULK DENSITY	The weight of one cubic foot of resin.
2)	COLUMN	A distillation column or tall vessel in which the separation or purification of chemicals takes place.
3)	COPOLYMER	A polymer such as VYHH produced from two monomers - vinyl chloride and vinyl acetate.
4)	IMPREGNATION	The act of adding a chemical such as isopropanol/water that causes a partial precipitation.
5)	INHERENT VISCOSITY	A measure of the molecular weight of a polymer.
6)	MOLECULAR WEIGHT	The sum of the atomic weights of the atoms in a particle. Typical atomic weights: Carbon = 12, Hydrogen = 1, Chlorine = 35.5, Oxygen = 16. Vinyl chloride (C_2H_3Cl) has molecular weight of (12 x 2) + (1 x 3) + (35.5 x 1) = 24 + 3 + 35.5 = 62.5. For vinyl resins the higher the molecular weight the more difficult the resin is to place in solution.

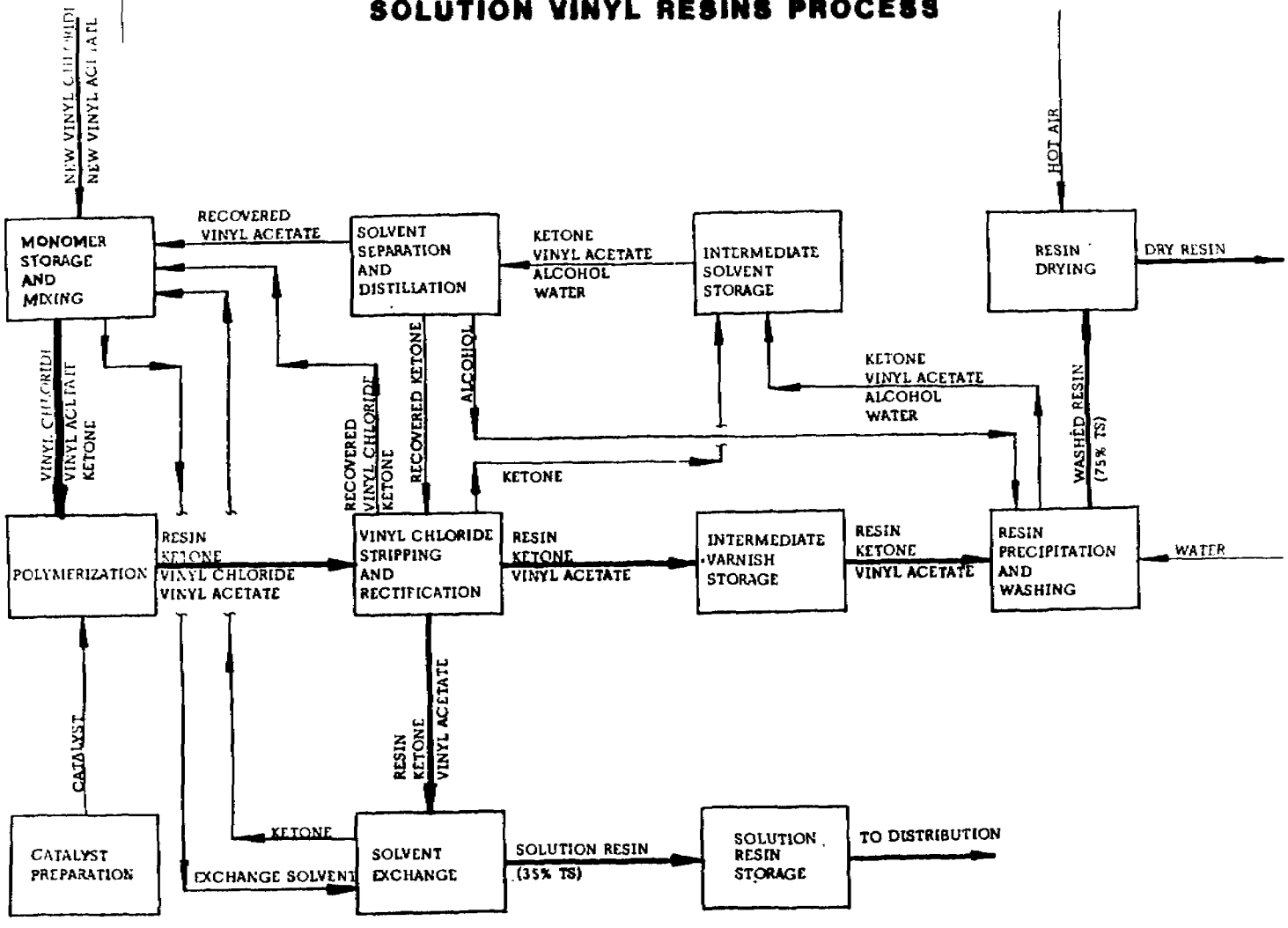
Glossary of Terms - continued

7)	MONOMER	A chemical capable of polymerizing to a polymer (resin).
8)	POLYMERIZATION	A chemical reaction in which two or more small molecules combine to form a large molecule called a "polymer".
9)	POROSITY	A measure of the size of the voids or open spaces found in resin particles.
10)	PRECIPITANT	A chemical or chemicals such as isopropanol/water that causes precipitation to occur.
11)	PRECIPITATION	The formation of solid particles from a solution.
12)	RECTIFICATION	The purification of vapor from a distillation process by the use of acountercurrent stream of liquid condensed from the vapor.
13)	SLURRY	A thin liquid containing suspended solid particles.
14)	SOLVENTS	A mixture of acetone, isopropanol, vinyl acetate and water produced in the resin precipitation unit that is the feedstock for the distillation unit.

Glossary of Terms - continued

15)	SPECIFIC GRAVITY	The weight of a material compared to the weight of water.
16)	STRIPPING	The removal of volatile components from a liquid mixture by passing a gas through the liquid mixture.
17)	TERPOLYMER	A polymer such as VMCH containing three monomers - vinyl chloride, vinyl acetate and maleic acid.
18)	VARNISH	The viscous, clear liquid formed when resin is placed in solution.

SOLUTION VINYL RESINS PROCESS



PROCESS DESCRIPTION

The Solution Vinyl Resin process consists of seven major identifiable operations as follows:

1) Autoclave Feed Preparation - Tank Area (T.A.) No. 1
2) Polymerization - Building 115
3) Varnish Stripping - Building 117
4) Solvent Exchange - Building 117
5) Resin Precipitation and Washing - Building 121
6) Resin Drying - Building 121
7) Solvents Recovery - Building 114

In T.A. No. 1 the acetone, vinyl acetate and vinyl chloride for autoclave feed are stored and mixed in the proper proportion so that when the monomers are polymerized in the autoclaves a resin is produced containing the correct amount of polyvinyl chloride and polyvinyl acetate and having the proper molecular weight.

The mixed feed is then pumped to the autoclaves at Building 115 where it is polymerized into vinyl resin kept in solution by the acetone. If other monomers such as maleic acid are required they are usually injected at the autoclave. Catalyst to promote the polymerization is also injected at the autoclave. Since all of the vinyl chloride and vinyl acetate are not polymerized to resin the mixture in the autoclave consists of acetone, resin, vinyl chloride and vinyl acetate. This mixture, called autoclave varnish, serves as the feedstock for the stripping unit.

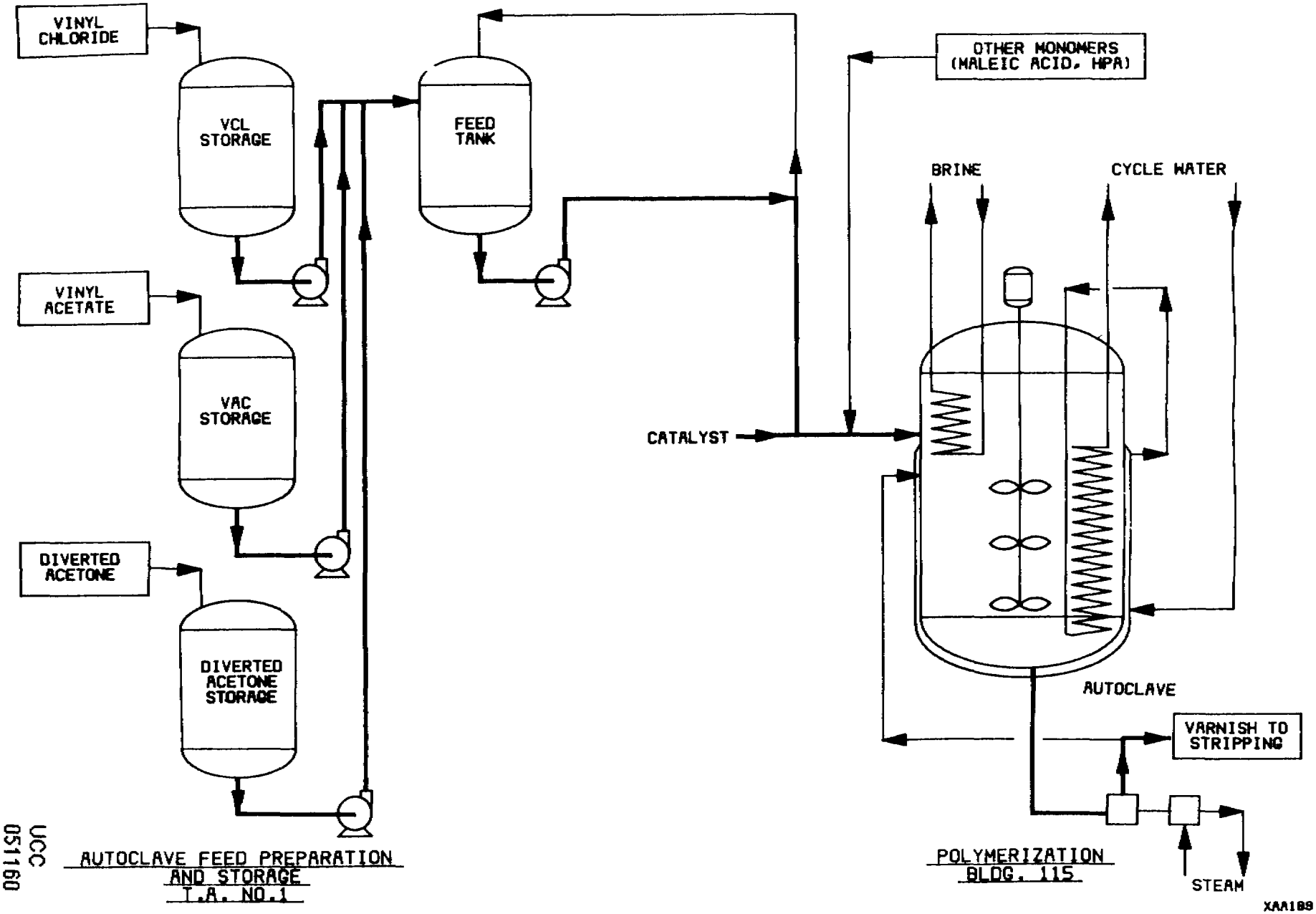
Process Description - continued

In the stripping unit all of the unreacted vinyl chloride and some of the unreacted vinyl acetate are removed from the varnish, now called "stripped varnish". Stripped varnish is then transferred to T.A. No. 2 and Building 122 for storage, or to the solvent exchange unit. Some vinyl resins are sold in solution rather than as a dry powder. Usually MEK and toluene are the desired solvents, so in the solvent exchange unit the acetone solvent and remaining unreacted vinyl acetate are replaced with a mixture of MEK and toluene.

When a dry powder is to be produced the stripped varnish is transferred to Building 121 where the resin is precipitated from the varnish by a mixture of isopropanol and water. After precipitation the resin remains suspended in a mixture of water, acetone, isopropanol and a small amount of vinyl acetate. Centrifugation is then used to separate the resin from this solvents-rich liquid. For additional solvents recovery the centrifuged resin is then washed by reslurrying in pure water. This slurry is again centrifuged, with the wet resin then being dried in a multi-stage hot air drying system and transferred to storage bins where it is held for packaging.

The "solvents" from the first stage of centrifugation are pumped to the distillation unit where, through a series of extraction and distillation steps, the vinyl acetate, acetone and isopropanol are recovered for reuse in the process.

SOLUTION VINYL RESINS PROCESS



TANK AREA NO. 1

RAW MATERIAL STORAGE AND AUTOCLAVE FEED PREPARATION

Here, the acetone, vinyl chloride (VCM) and vinyl acetate (VAc) are stored and mixed in the proper proportion for autoclave feed. Different resin types generally require different autoclave feed compositions. Maintaining the proper VCM to VAc ratio and the proper acetone concentration in the autoclave feed are extremely important if the desired resin compositions are to be achieved.

Flowing from the stripping unit to T.A. No. 1 is a mixture of acetone, VCM, and VAc called "diverted acetone". This stream usually supplies all of the acetone used in the autoclave feed but since it also contains VCM and VAc these components must be considered when setting the flows to the autoclave feed tanks. It is extremely important that the analysis of the diverted acetone be known and that the components be accurately accounted for so that the proper make up flows of pure VCM and VAc can be established to give the desired autoclave feed composition. Later, in the discussion covering the autoclave unit, the effect of varying feed compositions on resin properties will be covered. For this section let it suffice to say that the importance of maintaining the autoclave feed analysis exactly as specified cannot be overemphasized!

Certain contaminants are present in the autoclave feed that must be monitored. These are acetaldehyde, MEK and isopropanol. MEK enters the process via the solvent exchange still overhead when producing VYDS or VERR. The MEK ends up in the recovered VAc stream. Isopropanol is a contaminant in the recovered acetone and gets into the wrong places via blowback, equipment

Tank Area No. 1 Raw Material Storage and Autoclave Feed Preparation - continued

washing, stripping still acetone, etc. Normally, the MEK and isopropanol levels in the feed are so low that they can be ignored; but since they act similar to acetone in depressing molecular weight, their level in the feed must be watched.

Acetaldehyde is by far the worse contaminant with regard to its potential for causing problems in the autoclaves. An extremely small amount in the autoclaves can cause a significant drop in resin molecular weight. The normal concentration in autoclave feed is about 500 ppm (.05%). If the level rises above 1,000 ppm serious molecular weight control problems can occur. The usual source of acetaldehyde is the recovered acetone or vinyl acetate coming from the Distillation Unit.

BUILDING 115 - AUTOCLAVE (POLYMERIZATION) UNIT

Here, the various monomers such as VCM, VAc and maleic acid combine (polymerize) into resin and, if the right feed analysis is maintained and, if the autoclaves are operated properly, the desired resin analyses will result. If it is not done correctly in this step, that's it, we do not get another chance to change the resin monomer content or molecular weight (M.W.).

The autoclave operator has two major controls over resin properties - the temperature of polymerization and the degree of monomer conversion to resin. The M.W., or the size of the resin molecule, can be controlled by the reaction temperature. An increase in temperature reduces the size of the resin molecule resulting in a lower M.W. while a decrease in temperature increases the size and therefore, the M.W. Accurate control over M.W. is extremely important since it is a measure of how easily the resin can be placed in solution in various solvents. Solution vinyl resins are generally placed in solution by our customers and used in a coating application, so ease and uniformity of solubility are very important properties. Another parameter that can affect M.W. is the ratio of acetone to monomer in the autoclave. The more acetone relative to the monomer the lower the M.W., and conversely, the lower the acetone the higher the M.W. More on this further along.

VCM and VAc do not polymerize to resin at the same rate. If one were to take a pound of VCM and react it with a pound of VAc until all the VCM were consumed, the resin produced would not be 50 percent vinyl chloride (PVC) and 50 percent vinyl acetate (PVA). Rather, the product would be a

resin containing approximately 75 percent PVC and 25 percent PVA plus some left over monomeric VAc. Vinyl acetate reacts more slowly than vinyl chloride.

Feed from T.A. No. 1 that has been made to the proper analysis is added continuously to the autoclave along with catalyst that has been produced at Building 116, the catalyst manufacturing unit. The catalyst causes the monomers to polymerize. The more catalyst used, the faster the monomer reaction occurs, so the amount of resin being produced is controlled by the catalyst addition rate. Immediately upon entering the hot autoclave, monomer polymerization occurs due to the presence of the catalyst and the temperature. Not all of the monomers are polymerized to resin - generally about 48 percent of the VCM is converted to resin and about 30 percent of the VAc. A typical VYHH autoclave feed might be 56 percent VCM, 14 percent VAc and 30 percent acetone. One can see that in the feed 70 percent is monomer and 80 percent of the monomer $\left(\frac{56}{56 + 14}\right)$ is VCM. If VCM and VAc polymerized at the same rate this would produce a resin of 80 percent PVC. We know that this is not the case - the VCM is reacting faster than the VAc so that by the time 48 percent of the VCM has been polymerized and 30 percent of the VAc, a resin has actually been produced that contains 86 percent PVC and now the VCM in the autoclave is down to 74.6 percent of the total monomer. To maintain a constant PCV in the resin it is absolutely essential that the amount of monomer converted to polymer be kept constant. As the conversion changes, the ratio of VCM to VAc changes and therefore the PVC content of the resin changes.

Bldg. 115 - Autoclave (Polymerization) Unit - continued

Nothing happens to the acetone in the autoclave feed - a pound goes in and a pound comes out - it is there strictly to keep the resin in solution. However, as mentioned earlier, the molecular weight of the resin is influenced by the ratio of acetone to monomer. If the conversion of monomer to resin is not kept constant and the ratio of acetone to monomer changes, the molecular weight will also change. Suppose 50 percent of the VCM and 31 percent of the VAc are polymerized to resin rather than 48 percent and 30 percent as previously discussed. There will then be more resin in the autoclave and less monomer. The amount of acetone hasn't changed but since there is less unreacted monomer remaining, the ratio of monomer to acetone has decreased so that the molecular weight of the resin being produced will be decreased. Also, since the conversion of monomer to resin has increased, the ratio of VCM to VAc has changed so that a slightly different PVC content resin will also be produced. To summarize, as monomer conversion is increased the PVC content and the molecular weight of the resin are decreased.

How is the monomer conversion held constant? There are several measures available to determine the degree of conversion and to indicate changes as follows:

1) Mixed gravity on autoclave contents
2) Dynatrol continuous specific gravity reading
3) Autoclave pressure

EFFECT OF CHANGE IN FEED COMPOSITION AND AUTOCLAVE GRAVITIES ON RESIN PVC AND INHERENT VISCOSITY

Case	Feed Analysis Component, %		% VCM In Total Mon.	AUTOCLAVE CONTENTS: Monomer Conversion To Resin, %	Specific Gravity	Mixed Gravity	% VCM In Total Mon.	Monomer To Solvent Ratio	Approximate Effect on Resin: PVC, %	I.V.
I (Base Case)	VCM	56.0	80.0	48						
	VAc	14.0		30	1.003	.898	74.4	1.27	0	0
	Acet	30.0		-						
II	VCM	57.0	81.4	48						
	VAc	13.0		30	1.003	.898	76.2	1.27	+1.0	0
	Acet	30.0		-						
III	VCM	55.0	78.6	48						
	VAc	15.0		30	1.003	.898	72.7	1.27	-1.0	0
	Acet	30.0		-						
IV	VCM	54.4	80.0	48						
	VAc	13.6		30	1.001	.897	74.2	1.12	0	-.015
	Acet	32.0		-						
V	VCM	54.4	80.0	54						
	VAc	13.6		35	1.008	.900	73.8	1.06	-0.4	-.020
	Acet	32.0		-						
VI	VCM	56.0		40						
	VAc	14.0	80.0	24	0.980	.886	75.7	1.44	+0.7	+.018
	Acet	30.0		-						

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Bldg. 115 - Autoclave (Polymerization) Unit - continued

Vinyl resin has a very high specific gravity (1.3) compared to the other materials in the autoclave so a change in resin content can be readily determined by measuring the specific gravity of the autoclave contents. Nos. 1 and 2 above utilize this property to determine the amount of resin in the autoclave, which, of course, is also a measure of the amount of monomer conversion.

Most of the pressure in the autoclave is due to the presence of VCM. Pure VCM at 60°C exerts a pressure of 160 psig while pure acetone and vinyl acetate have vapor pressures of only 24 and 31 psig, respectively. The pressure in a VYHH autoclave at 60°C with the normal 48 percent VCM and 30 percent VAc conversions would typically be 56 psig with 85 percent of that due to the VCM. So, it can be readily seen that pressure can also be used to indicate the degree of VCM conversion to resin.

The Dynatrol is the technique used for measuring monomer conversion and the others are merely guides in the event the Dynatrol malfunctions or appears to be operating improperly. Via laboratory analyses of the actual autoclave contents the desired Dynatrol reading will be specified for each resin type and each autoclave. These specified readings must be maintained as closely as possible since a change of two lines on the chart equals a change in specific gravity of 0.004. This slight apparent change can cause the PVC to change by 0.12% and the I.V. by .002.

In the above table are several examples to show the effect on resin properties with varying feed analyses and degrees of conversion.

Case I is the base case, the desired conditions.

Case II shows the effect on resin analyses when the VCM content of the feed increases 1 percent and the VAc content decreases 1 percent. Note that the PVC increases 1.0 percent.

Case III reverses the situation with VCM in the feed being decreased by 1 percent and the VAc increased by 1 percent. As expected, the PVC decreases by 1.0 percent.

In Case IV the acetone in the feed has increased by 2 percent causing a drop in Inherent Viscosity (I.V.) which means that a drop in molecular weight has occurred.

In Case V not only is the acetone in the feed 2 percent high but the conversion of monomer to resin is greater than the base case so that the net effect is a drop in both PVC and I.V.

Case VI illustrates the effect when monomer conversion is low even though the feed analysis is o.k. Note that PVC and I.V. are both increased.

Bldg. 115 - Autoclave (Polymerization) Unit - continued

The autoclaves should be operated at high monomer conversion. However, too high a conversion (too much resin in the autoclave) can cause the autoclave contents to become so viscous that agitation, pumping ability and heat transfer will be lost. We certainly want to avoid that situation so this is another reason why autoclave conditions must be closely monitored and the specified Dynatrol reading maintained. High monomer conversion improves vinyl acetate efficiency and reduces the amount of unreacted vinyl chloride that must be recovered in the stripping unit. Frequently, autoclaves will be operated in series which is usually nothing more than a technique to increase the conversion of vinyl acetate. The lower the vinyl acetate in the autoclave varnish feeding the stripping unit the less there will be in the stripped varnish. The lower the vinyl acetate in the stripped varnish the less will be lost in the downstream units and the easier the resin will be to dry in Building 121.

After a certain number of hours of operation, autoclaves must be washed with hot acetone to remove "gel" formations from the cooling coils and other autoclave internals. When the wash is finished it must be cooled prior to pumping to T.A. No. 3; otherwise, much of the hot acetone will be lost from the tank vent, plus creating a hazard when the hot acetone vapors vent to the atmosphere.

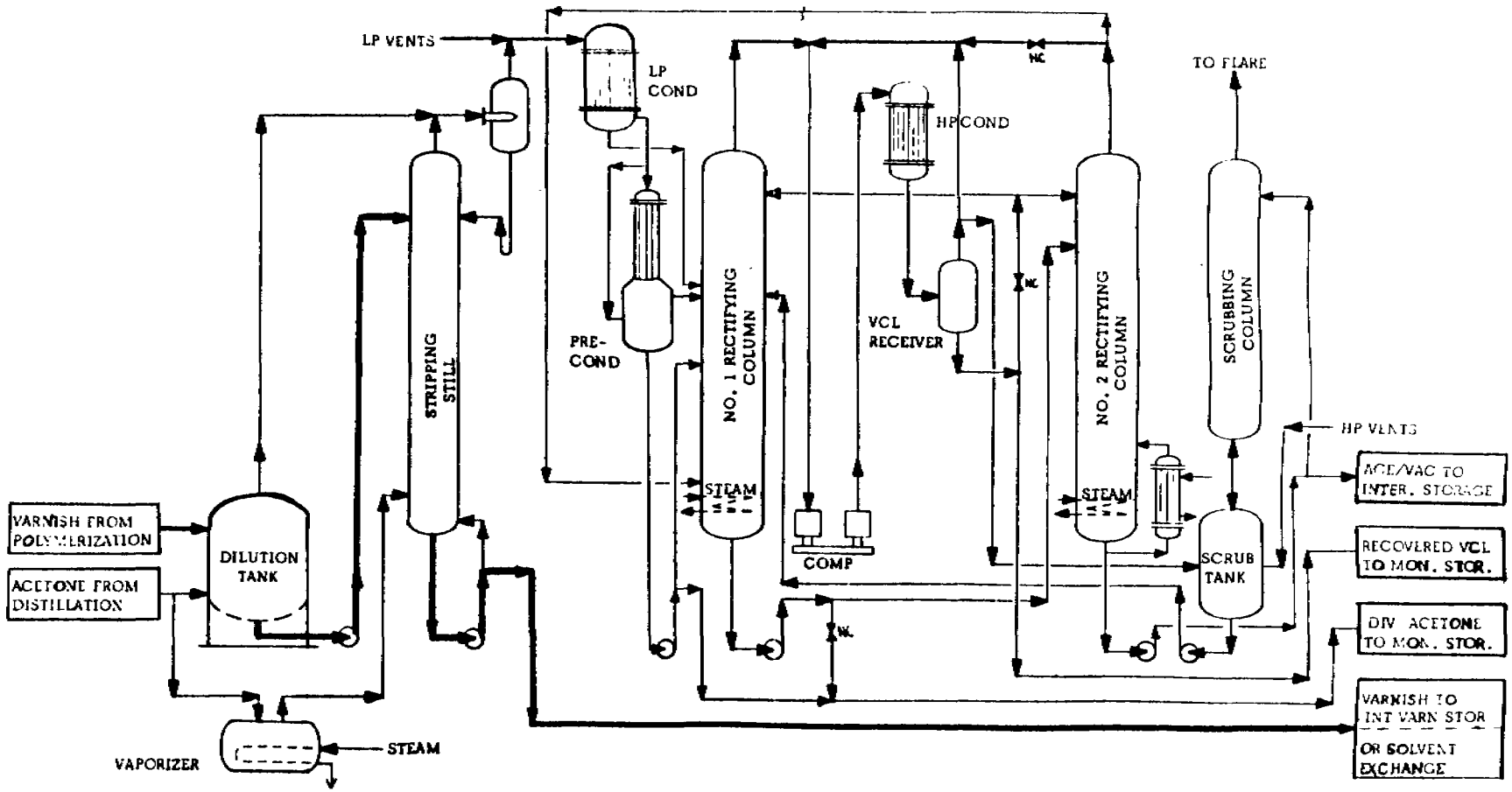
Catalyst addition rates are generally left up to the discretion of the operator with the controlling factor being the amount of varnish being processed at the precipitation unit. Rapid increases in catalyst addition should be avoided since reaction response may not be immediate.

Bldg. 115 - Autoclave (Polymerization) Unit - continued

The reaction rate might not increase significantly until a considerable amount of catalyst has been added and then in a rather short period of time polymerization can increase dramatically, possibly exceeding the cooling capacity of the autoclave. If this occurs, temperatures and pressure will rise requiring implementation of emergency procedures. Compounding the situation due to the amount of resin being produced, an increase in the viscosity of the autoclave contents may occur, reducing heat transfer capability and stopping pumping to the stripping unit. Always observe the maximum catalyst addition rate as specified in the S.O.P.'s.

From all of this one can see that to produce exactly the desired resin the autoclave feed analysis must be precisely correct, the autoclave temperature must be held constant, and the degree of monomer conversion to resin must also be constant.

SOLUTION VINYL RESINS PROCESS



VINYL CHLORIDE/VINYL ACETATE

STRIPPING AND RECTIFICATION

BLDG. 117

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BUILDING 117 - STRIPPING AND RECTIFICATION

Varnish from the autoclaves is pumped to the stripping unit where the unreacted vinyl chloride is removed and the varnish gravity adjusted according to the needs of the resin precipitation unit.

The first piece of equipment the autoclave varnish enters is the dilution tank. Here most of the VCM boils off due to the reduction in pressure. The VCM is replaced with dilution acetone to maintain proper viscosity as the solids increase due to removal of the VCM. Wash acetone or new acetone are generally used for dilution. The amount of dilution determines the specific gravity of the varnish leaving Building 117.

Varnish gravities should be maintained on the high side of the Building 121 request. The varnish can be diluted at Building 122 to the level requested by Building 121 but it cannot be increased in gravity; so, if it leaves the stripping unit on the low side that's what the precipitation unit will have to work with. High varnish gravities mean less acetone to be recovered and therefore less load on the Distillation Unit. Also, since there will be less acetone in the cycle and losses will be reduced.

From the dilution tanks the varnish is pumped to the stripping still where the remaining VCM is removed. Also, in the stripping still some of the unreacted VAc is removed, the amount depending on the volume of acetone vapors sparged to the base of the still. It is imperative that enough acetone vapor be used to remove all of the VCM so that none goes with the varnish, causing air

Bldg. 117 - Stripping and Rectification - continued

pollution problems in the downstream units. Acetone vapors over and above that required for VCM removal can be added to reduce the VAc content of the stripped varnish. Generally speaking, residual VAc in the varnish should be held below 5.0 percent to minimize VAc losses and reduce the problems that it causes in the resin precipitation, drying area. Follow the S.O.P.'s for the desired acetone vapor flows for each resin type.

Coolers are provided for the stripped varnish pumped to the T.A. No. 2 varnish storage tanks. These tanks operate at atmospheric pressure. The temperature of the varnish leaving the base of the stripping stills is above the boiling point of acetone at atmospheric pressure; so, if the varnish is not cooled, some of the acetone will boil off and possible be lost to the atmosphere.

Leaving the top of the stripping still is a mixture of VCM, VAc and acetone. This vapor mixture first passes through the "low pressure" cycle-water cooled condensers and then into the brine cooled pre-condenser. In the pre-condenser the acetone, VAc and some of the VCM are condensed. Uncondensed VCM passes into the No. 1 rectifying column for recovery. The liquid in the base of the pre-condenser consists of a mixture of acetone, VCM and VAc which becomes the diverted acetone stream mentioned in the T.A. No. 1 discussion that is the acetone supply for the autoclave feed stream. More diverted acetone is produced than can be used in the autoclave feed so the excess goes to the No. 1 rectifying column where most of the VCM is removed. The base of the No. 1 rectifying column is then pumped to the No. 2 rectifying column where all of the remaining VCM is

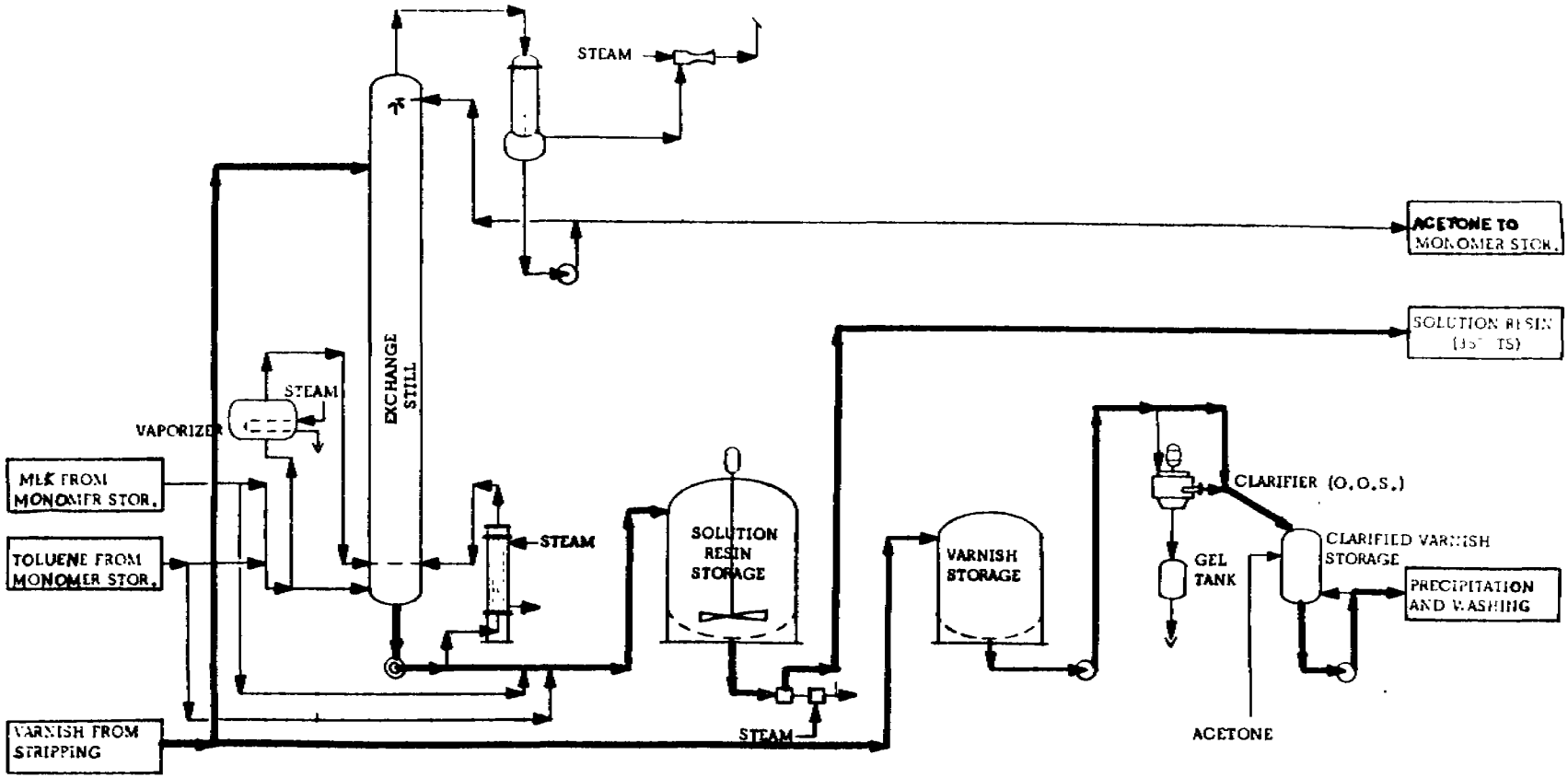
Bldg. 117 - Stripping and Rectification - continued

removed. Recovered VCM is returned to T.A. No. 1 for use in the autoclave feed. The acetone, VAc mixture in the base of No. 2 rectifying column is pumped to T.A. No. 2 where it mixes with the solvents coming from the precipitation unit for recovery at the distillation unit.

This diverted acetone stream transferred to T.A. No. 2 can, by the time it is mixed with water, amount to considerable load on the distillation unit. Usually, the distillation unit is taxed just to recover the solvents produced in the resin precipitation process, so the diverted acetone stream pumped to T.A. No. 2 can cause an overload at the distillation unit and necessitate a reduction in resin production. Therefore, we want to keep the diverted acetone stream being pumped to T.A. No. 2 at a minimum. Diverted acetone production is reduced by operating the autoclaves at high conversion and by not using excessive acetone vapors on the stripping stills. Follow the S.O.P.'s for the correct acetone vapor (L/V's) to be maintained.

Recovered VCM contains some acetone. The acetone can vary depending on the No. 1 rectifying column head temperature. It is important that the specified temperature be maintained so that the acetone in the VCM is constant. This acetone is being allowed for in the preparation of the autoclave feed so variability in the feed analysis will result if there is variability in the recovered VCM acetone content.

SOLUTION VINYL RESINS PROCESS



SOLVENT EXCHANGE SYSTEM
BLDG. 117

VARNISH STORAGE AND CLARIFICATION
T.A. NO. 2, BLDG. 122

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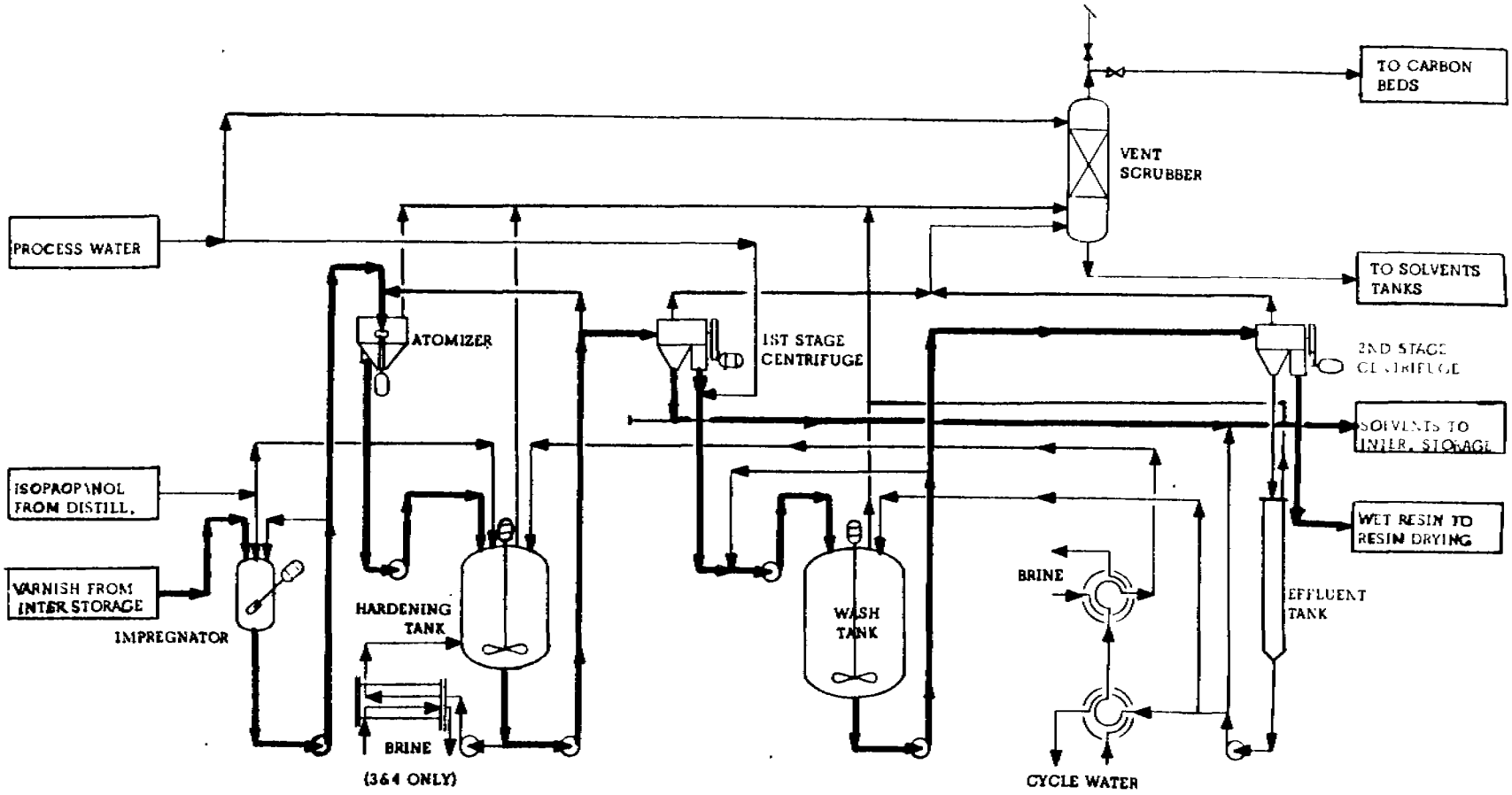
SOLVENT EXCHANGE UNIT

As mentioned in the Introduction this unit supplies resin to our customers in solution rather than in dry powder form. Varnish from the stripping still is pumped to the solvent exchange still where the acetone solvent is replaced with a higher boiling solvent, usually toluene and methyl ethyl ketone (MEK). It is important that good removal of VCM occur both in the stripping still and the exchange still so that the final product contains less than 10 ppm of VCM.

T.A. NO. 2, BUILDING 122

The large varnish storage tanks located in T.A. No. 2 are to provide surge capacity between the autoclave/stripping units and the precipitation unit in Building 121. Small "inside" varnish tanks are located at Building 122 where the varnish gravity is adjusted to satisfy the needs of the precipitation unit. All of these tanks operate at atmospheric pressure. The tanks are equipped with vent headers connected to brine cooled condensers. It is important that these vent headers, condensers and nitrogen blanketing systems be checked periodically for proper operation so that acetone that boils off the warm varnish will be condensed and returned to the tanks rather than being vented to the air. The Building 122 operator should keep close watch over the varnish gravities and strive to provide the precipitation unit with the correct gravities. The precipitation unit operator should be notified when changes in varnish gravities occur since the operation of the precipitation/drying unit will be affected.

SOLUTION VINYL RESINS PROCESS



RESIN PRECIPITATION, HARDENING AND WASHING

BLDG. 121

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BUILDING 121 - RESIN PRECIPITATION, HARDENING AND WASHING

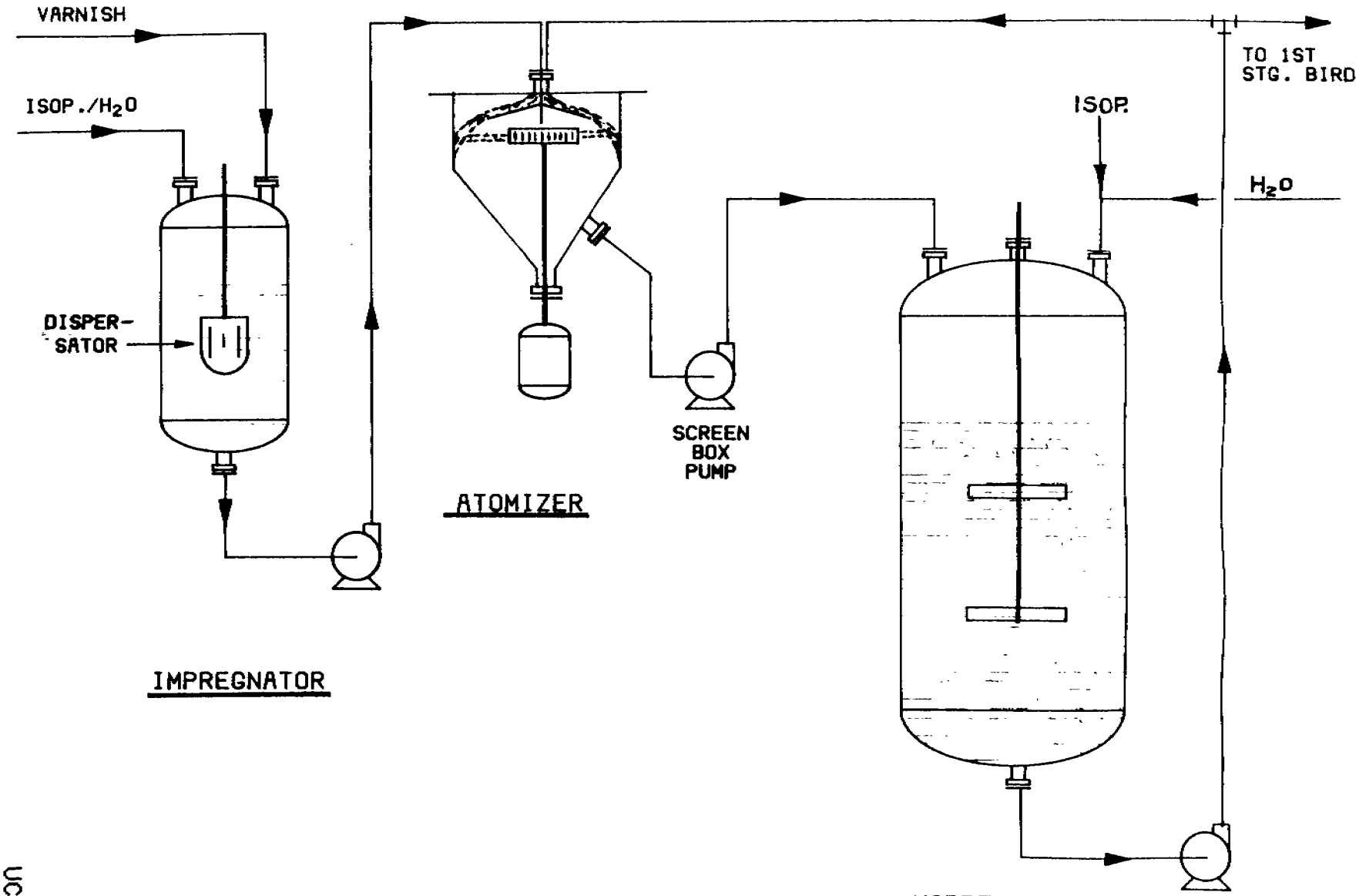
Varnish from Building 122 first enters a small, highly agitated vessel called the Impregnator. The purpose of the Impregnator is to partially precipitate the resin from solution using a mixture of isopropanol and water. Agitation in the Impregnator is provided by a Dispersator, which is nothing more than a high capacity pump that serves as an efficient mixer and agitator. The Dispersator intimately mixes the isopropanol/water with the varnish and keeps the partially precipitated resin in suspension. Important Impregnator operating variables are:

1) Varnish Gravity - Maintain gravities as high as the system will tolerate. The less acetone in the system the fewer problems will be encountered in the hardening tank and first stage Bird. Also, the load on the distillation unit will be reduced. However, if varnish gravities become too high, control over impregnation becomes difficult due to the viscosity of the mixture and a large or a particle having low porosity that is difficult-to-dry will be produced.

2) Varnish Temperature - Low varnish temperatures will cause the production of low bulk density resin. If the temperature is low in conjunction with a high gravity the high viscosity in the Impregnator will prevent good mixing and cause the production of large, irregular shaped particles low in bulk density and difficult to dry.

"Goodness" is on the side of high varnish gravities and temperatures! Different resins require different gravities and temperatures for optimum precipitation/drying conditions so the S.O.P.'s should be consulted for specific conditions.

SOLUTION VINYL RESINS PROCESS



RESIN PRECIPITATION AND HARDENING SYSTEM - BLDG. 121

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Bldg. 121 - Resin Precipitation, Hardening and Washing - continued

3) Isopropanol Gravity - The isopropanol used at Building 121 is actually a mixture of isopropanol, water and acetone. A typical analysis would be 56 percent isopropanol, 36 percent water and 8 percent acetone having a gravity of 0.865. Recent findings indicate that the water is the real precipitant with the isopropanol primarily acting as a surfactant[1] to reduce the surface tension of the water simplifying control over impregnation, precipitition, particle size control, and particle porosity. If water, then, is the real precipitant one can readily see how important it is that the amount of water in the "isopropanol" be kept constant.

4) Isopropanol Temperature - As with varnish temperature, "goodness" is toward the high side so that good mixing with the varnish is obtained. Cold isopropanol mixed with warm varnish can reduce mixing by increasing the viscosity of the impregnated varnish.

Although "goodness" is generally toward the high side on varnish gravities and temperatures, the difficult to precipitate, low M.W. resins will sometimes require that varnish gravities and temperatures be lowered to effect precipitation. Specific temperatures, gravities, etc. for the streams feeding to the Impregnator cannot be supplied here. Different resins such as VYNS, VYHH,

[1] K. W. Wang, "Solution Vinyls Recovery Without Isopropanol: Laboratory Feasibility Studies of VMCC and VYHH Resins", May 21, 1981.

Bldg. 121 - Resin Precipitation, Hardening and Washing - continued

VMCH, VYHD and VMCC require different conditions for optimum particle control and drying rates. Conditions at the autoclave and stripping unit can influence the optimum operating conditions in the precipitation unit. Operating ranges will be supplied in the S.O.P.'s but the important message is that the operator understand the effect of the variables so that optimum conditions can be established and corrective changes made as conditions change.

From the Impregnator the varnish is pumped to the atomizer where the final precipitation occurs. The atomizer is a slotted wheel about 6-inches in diameter rotating at 14,000 RPM. Varnish is fed into the center of the wheel and "thrown out" through the slots in droplet form. The higher the varnish viscosity and the higher the varnish feed rate the larger the droplet will be. If the resin from an individual droplet leaving the atomizer were precipitated it would be quite small, much smaller than the optimum size particle for the drying system.

During the production of low molecular weight resins such as VMCC, the atomizers may not be used. The present state of the art requires that in order to produce a porous resin which can be dried at good rates, a low varnish gravity and lots of isopropanol must be used. This low gravity, coupled with the excess isopropanol in the impregnator, causes essentially total precipitation to occur. Under these conditions if the atomizers are used, too fine a particle will be produced. One of the major technical efforts in the future will be to try to increase the varnish gravity on low molecular weight resins and this may lead to use of the atomizers. The other major technical effort will probably be directed toward reducing the isopropanol used on all resins.

Bldg. 121 - Resin Precipitation, Hardening and Washing - continued

RESIN HARDENING

The thrown-out droplets of impregnated varnish from the atomizers strike a falling film of relatively cold water (slurry from the hardening tank) where the final precipitation occurs. From the atomizer "tub" the resin slurry, before entering the hardening tank, passes through a grinder called a screen box pump to break up any lumps that have fallen off the walls of the "tub". Cold water is added to the hardening tank to provide the slurrying medium for the resin and to act as the final precipitant.

The resin slurry in the hardening tank is recycled to the atomizer tubs to provide the falling film of "water" for final precipitation and is pumped to the first stage Bird where the solvent-rich liquid stream is separated from the resin by centrifuging.

Hardening tank operating conditions are crucial in controlling resin particle size and porosity. The small particles produced by the atomizer must be agglomerated (stuck together) to produce the ultimate particle that performs properly in the drying system. This agglomeration occurs as a result of hardening tank temperature and the amount of acetone present. The higher the temperature and the more acetone present the greater will be the agglomeration.

This can be carried too far. Particles can become too large for good drying and/or excessive oversize tailings will be produced in the air-separator. For best drying rates the resin must be porous (resemble a sponge) so that the moisture trapped in the particle can find a way to the

surface where it is removed by the hot, dry air. A 90 micron size particle made by sticking a number of small particles together will have more porosity and be more easily dried than one particle of 90 micron size.

Another limit on the temperature and acetone concentration in the hardening tank is the performance of the first stage Bird. If the resin is too soft, caused by either too high an acetone concentration or too high a hardening tank temperature, it may plug the Bird or come out in such large lumps that the wet grinder installed to break up the lumps from the Bird will plug. Generally, it should not be necessary to add isopropanol to the hardening tank. There should be enough isopropanol coming in from the Impregnator to suffice. There is some evidence, however, that when the VAc in the varnish is high that extra isopropanol added to the hardening tank helps in particle size control and hardening. Preferably, isopropanol is kept "off" the hardening tanks - the more used the more lost throughout the process.

RESIN WASHING

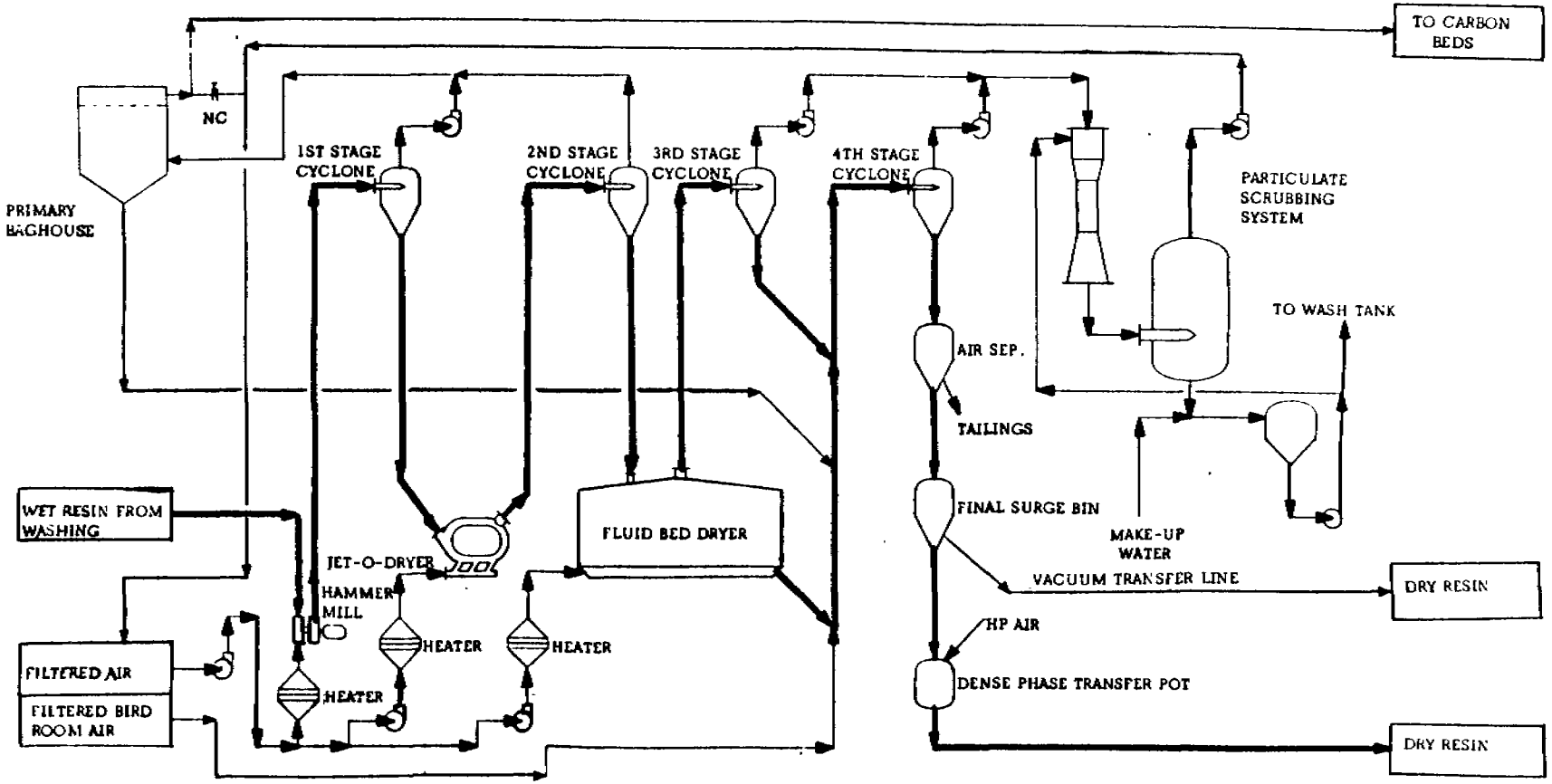
The centrifuged resin from the first stage Bird contains considerable trapped solvents which should be recovered before the resin enters the hot air drying stages. Two techniques are used to recover these solvents: 1) washing with pure, fresh water and 2) temperature. The resin exiting from the Bird is immediately reslurried with pure water and passes through a grinding pump called the "wet grinder" to break up any lumps formed in the Bird. This pump discharges into the wash tank. The wash tank is a means of providing enough contact time that the solvents trapped in the resin particles can be extracted by the water. The temperature in the wash tank is maintained as

high as possible without the resin becoming so soft that second stage Bird centrifuging problems result. The speed of solvent extraction from the resin particles is controlled by the concentration of solvents in the water. As the solvents in the water increase, the "driving force" responsible for moving the solvent from the interior of the particle to the surface decreases. So, it is important to keep the temperature of the water (slurry) in the wash tank as high as possible, so that the solvents (primarily acetone) are boiled away. Maximum wash tank temperatures depend on the resin type. Typical temperatures would be 70°C for VYNS, 60°C for VYHH and 40°C for VMCH.

The solvents boiled out of the wash tank pass through a vent header system to a scrubber utilizing cold water to absorb and condense the solvents. If the vent header is plugged, the pressure in the wash tank will merely increase and the solvents will probably be leaked to the air. It is extremely important that the vent header from the wash tank to the scrubber be clean. A properly operating vent header will feel warm to the touch. It is just as important that an adequate supply of cold water be used on the scrubber and that the packing (Raschig rings/saddles) be clean. The vent scrubber and its drain line should be cool to the touch and in the summer it will usually "sweat". If the scrubber is not operating properly the solvents will pass out the vent to the atmosphere or to the carbon adsorbers.

From the wash tank the resin slurry is pumped to the second stage Bird. The resin from the Bird then enters the hot air drying system while the liquid becomes the supply of water for the hardening tank.

SOLUTION VINYL RESINS PROCESS



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RESIN DRYING (LINES 3 AND 4)

BLDG. 121

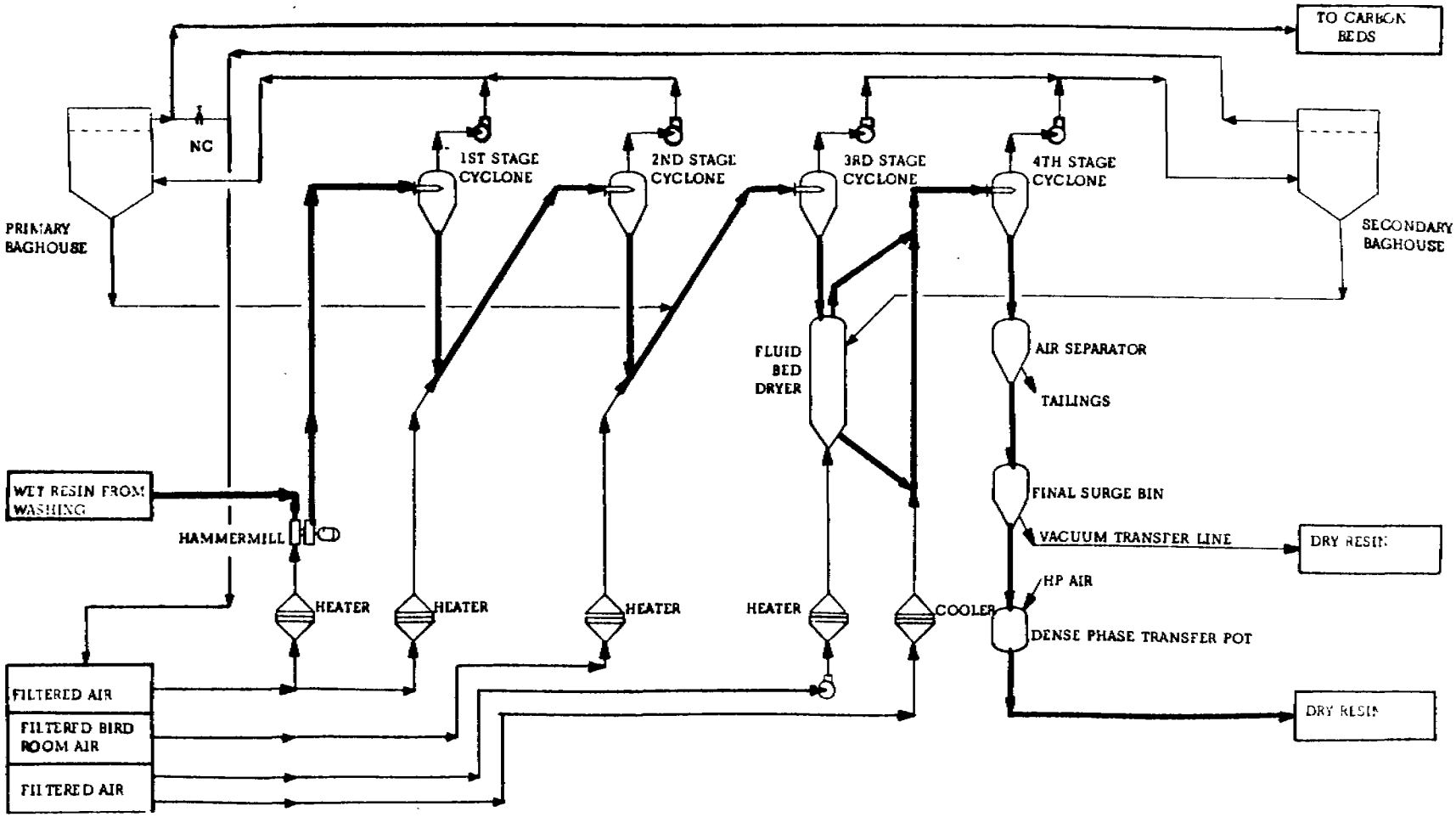
BUILDING 121 - RESIN DRYING

Resin exiting from the second stage Bird will usually contain 20-30 percent moisture. The higher the wash tank temperature the lower will be the volatiles. The high temperature apparently increases the plasticity of the resin so that under the influence of the centrifugal force in the Bird, more liquid is "squeezed" out. Anyway, for whatever reason, that's the way it works - high wash tank temperatures invariably increase drying rates due to the higher Bird solids. Between the Bird and the first stage of drying is a rotary valve serving as a seal so that solvent vapors under slight pressure in the bird will not be drawn into the vacuum that exists where the resin enters the first stage of drying. Bird hopper plugs that occur above this rotary valve are also reduced by operating at elevated wash tank temperatures. The drier the Bird resin the more free flowing and the less tendency it has to "cake" above the rotary valve.

The first stage of drying occurs in a hammer mill installed to break up the lumps caused by compaction in the centrifuge. Hot air and resin enter at one end of the mill, pass through the grinding section, through an integral fan and then into the discharge ducts that lead to the first stage cyclone. Most of the drying occurs in this first stage.

In drying, the most important temperature to be watched is the temperature that the resin itself is elevated to as measured by the cyclone or fluid bed dryer (FBD) outlet temperatures. If this temperature is too high the resin becomes soft, causing duct work, cyclone and FBD plugs. As long

SOLUTION VINYL RESINS PROCESS



RESIN DRYING (LINES 1 AND 2)

BLDG. 121

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Bldg. 121 - Resin Drying - continued

as there are volatiles in the resin to be flashed off the resin will be cooled by the vaporization. As the resin becomes drier in the stages downstream of the first stage, hot air inlet temperatures must be decreased to prevent the resin temperature from becoming excessive. In the first stage, air inlet temperatures of 100-120°C can be tolerated; in the second stage of drying these temperatures usually cannot exceed 90-100°C, while in the third stage or FBD the air inlet temperatures usually cannot exceed 70-80°C. As the resin becomes drier it becomes more difficult to remove the last few percent of volatiles. It takes more time to extract the moisture than is available in a flash drying stage where the contact time is only seconds. Consequently, the FBD's were installed. They are designed to operate with a bed of resin being fluidized by warm air so that enough contact time exists between the air and the resin to allow additional volatiles trapped in the resin particle to migrate to the surface where it is removed by the air. In the FBD's on Nos. 1 and 2 systems, if operated half full of resin, the contact time will be about 15 minutes while in the large FBD's on Nos. 3 and 4 systems the average contact time is 30 minutes to an hour. The Jet-O-Driers installed as the second stage of drying on Nos. 3 and 4 systems are nothing more than flash dryers providing a little more contact time than the traditional flash drying stages such as the second and third stages on No.s 1 and 2 systems.

For good drying rates it is necessary that a particle be produced in the precipitation step that distributes the drying load over each of the drying stages. Too fine a particle will load up or,

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Bldg. 121 - Resin Drying - continued

as we say, "bog down" the first stage of drying and subsequent stages will be idle. Too large a particle will be obvious when none of the stages are loaded, the resin is not dry and excessive tailings are being produced in the air separator. If the proper size, porous particle is being produced each of the drying stages will be carrying some of the load (as measured by the difference between the air inlet and cyclone outlet temperatures), tailings production will be low and the resin will be dry. This then becomes the criteria that is controlling the precipitation steps - we are trying to produce a particle of the proper size that can be dried.

When drying problems are encountered that defy correction by the usual techniques and the problem seems to be general across all the systems, check the isopropanol for nonane. Nonane in the isopropanol will be absorbed by the resin and not removed in the washing and drying stages. When nonane is observed in the isopropanol contact the Building 114 operator immediately.

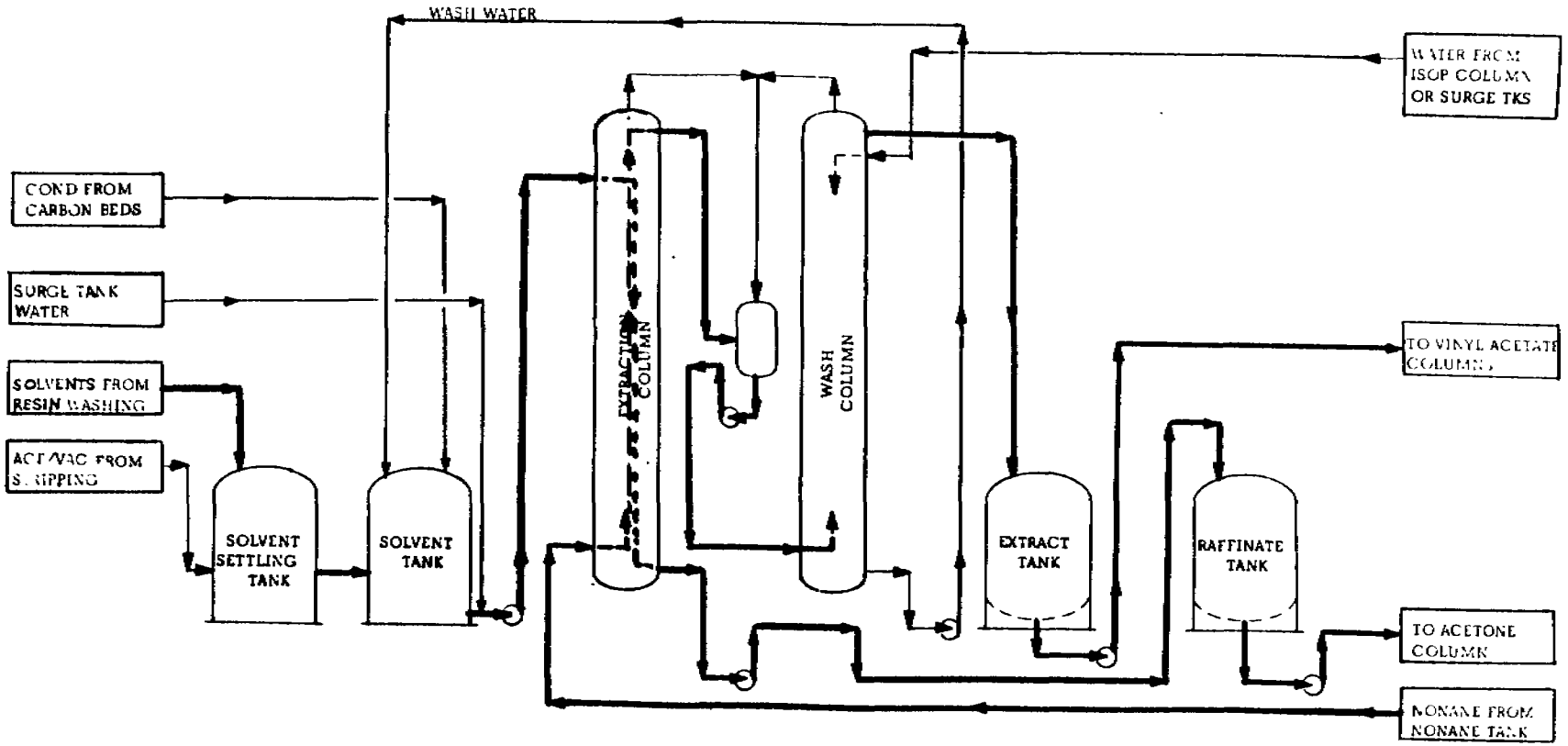
Also, watch the isopropanol gravity. A Dynatrol is installed by the impregnator on No. 1 system for measuring the gravity in the main supply header coming from Building 114. The gravity is used as a measure of the amount of water in the isopropanol. Remember that water is the precipitant and a little bit goes a long way. An 0.865 gravity isopropanol contains 35% water and 0.850 gravity contain 30% water. A 5% change in isopropanol water content doesn't seem like much but keep in mind that it is a 15% change in concentration and it will have a pronounced effect on the

Bldg. 121 - Resin Drying - continued

degree of precipitation that occurs in the impregnator. The Building 114 operator now has a Dynatrol for controlling the water content of the isopropanol, so in the future the quality should be much more consistent. Watch your isopropanol quality closely - it's an important variable!

To summarize the Building 121 operation, art rather than science has been practiced in the past because we just were not controlling or measuring the variables that were affecting the operation. It's hard to imagine a worse control problem. Now that the reaction phase of the process is under better control, the variables affecting Building 121's performance such as PVC, I.V., varnish gravity and residual vinyl acetate in the varnish are under better control so that now the effect of varnish temperature, isopropanol quality, etc. can be meaningfully evaluated. Within the near future, we should be able to prescribe precise operating conditions for Building 121 for each resin type.

SOLUTION VINYL RESINS PROCESS



INTERMEDIATE SOLVENT STORAGE

T.A. NO. 2

VINYL ACETATE EXTRACTION,

EXTRACT WASHING

BLDG. 114

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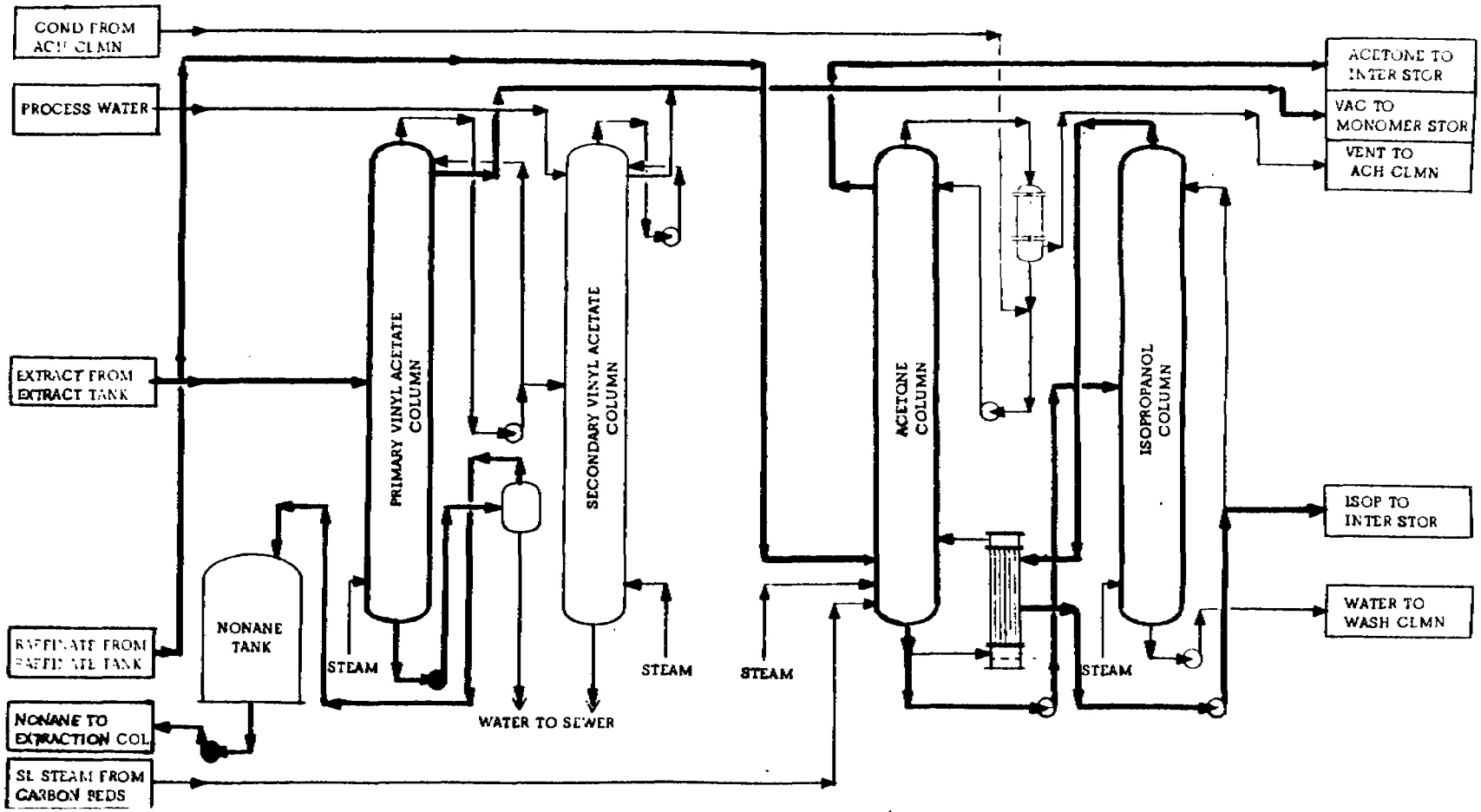
BUILDING 114 - DISTILLATION

The solvent-rich streams from the first stage Birds in Building 121 flow to intermediate storage tanks in T.A. No. 2 that provide surge capacity between the precipitation process and the distillation unit. It also provides a place where the specific gravity of the solvent stream can be adjusted if necessary for proper performance of the extractors at Building 114. The solvents stream has an approximate analysis of 67 percent water, 20 percent acetone, 10 percent isopropanol and 3 percent vinyl acetate. The ability to separate products by distillation techniques requires a reasonable difference in boiling temperatures of the materials to be separated. The boiling temperatures at atmospheric pressure of the organics in this stream are as follows:

	°C
Acetone	56.1
Vinyl Acetate	72.7
Isopropanol	82.3

It would be extremely difficult to separate these components by a straight distillation process and further complicating the matter is the property of vinyl acetate and isopropanol to form azeotropes with water. These azeotropes, or water mixtures, do not boil at the same temperature as the pure chemical, further complicating the separation process. For instance, the vinyl

SOLUTION VINYL RESINS PROCESS



VINYL ACETATE RECOVERY

BLDG. 114

ACETONE/ISOPROPANOL RECOVERY

50, 60 AND 70 COLUMNS

BLDG. 114

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Bldg. 114 - Distillation - continued

acetate/water azeotrope boils at 66°C (the composition is 93 percent VAc and 7 percent water). This is so close to the boiling point of acetone at 56°C that it becomes a very difficult separation. The spread between acetone and isopropanol is great enough that separation by distillation is relatively simple. So, to simplify the recovery of these materials a scheme was devised to selectively extract the vinyl acetate from the solvents stream leaving only the acetone, isopropanol and water to be separated.

The solvents first pass through an extractor where nonane, which is similar to kerosene, is used to extract the vinyl acetate. The two streams pass counter-currently in the liquid filled extractor with the heavy solvents stream (specific gravity of 0.945) entering near the top and the nonane (specific gravity of 0.719) entering near the bottom. As the light nonane rises to the top of the extractor it absorbs the vinyl acetate from the solvents stream flowing down the extractor. To enhance separation of the nonane and solvents a good differential must be maintained between the gravity of the two streams. At times, extra water will be added to the solvents at T.A. No. 2 to maintain the proper gravity.

A small percentage of acetone and isopropanol absorbed into the nonane extract must be removed and again an extraction process is employed. In another column (called the wash column, identical to the nonane extractors) water is used to extract the acetone and isopropanol so that leaving the wash column from the top is a pure mixture of nonane and vinyl acetate, while coming out of the bottom is the water containing the acetone and isopropanol. This "wash water" flows to T.A. No. 2

Bldg. 114 - Distillation - continued

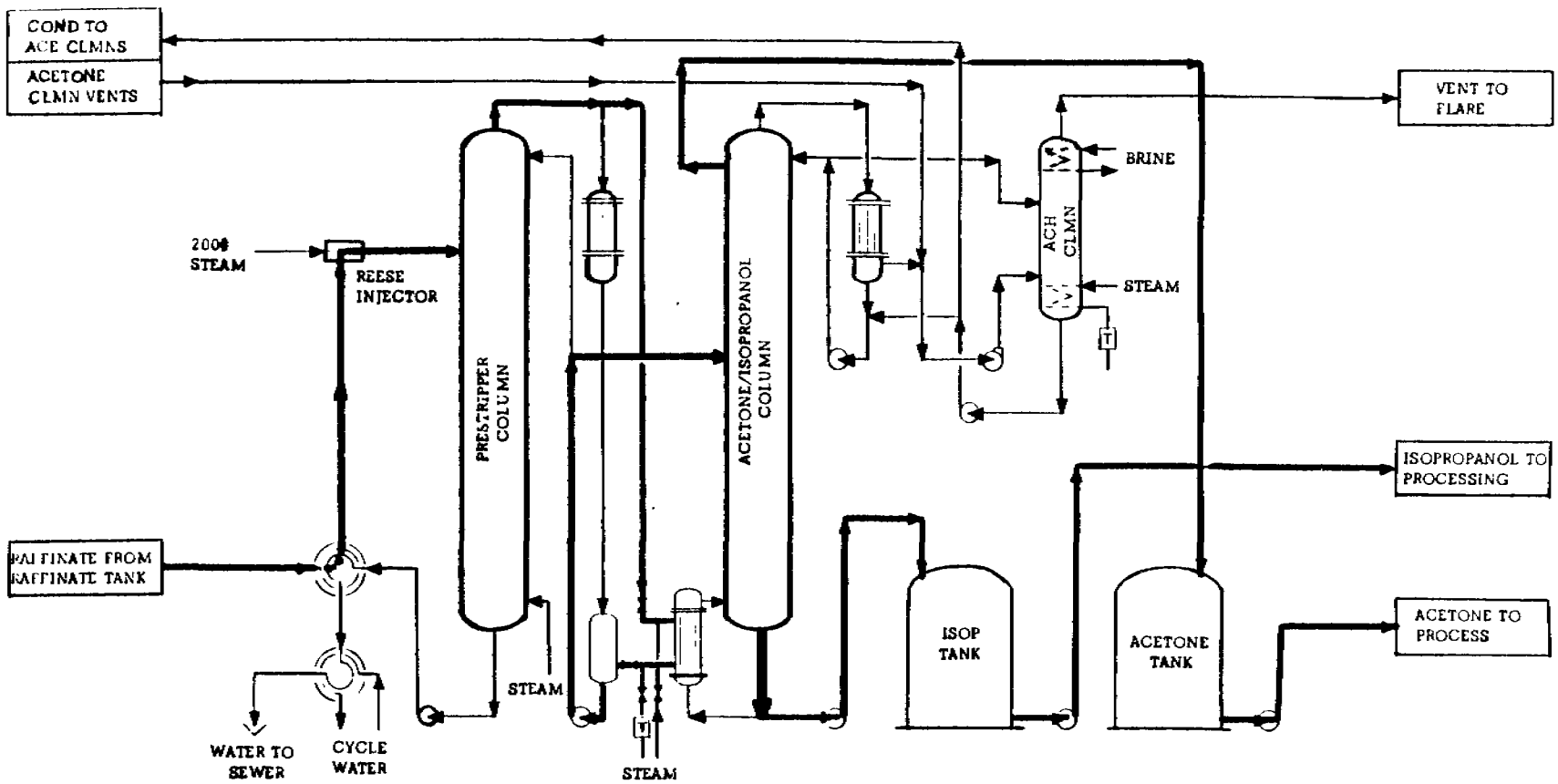
to join the solvents stream and serves to raise the gravity of the solvents to the desired level. It is important that the temperature of the water used on the wash column not exceed 50°C, otherwise, the acetone will be boiled off and lost to the atmosphere through the column vent. Since wash water is usually the tails stream from an isopropanol column operating at 150°C if the heat exchangers used to cool the water are fouled, the water can be considerably above 50°C, so this should be closely monitored.

It is also extremely important that the correct amount of water be used on the wash column. This flow should be at least 45 MLB/Hr. If the flow drops too low, acetone will stay in the extract and go out with the recovered vinyl acetate. This causes problems in T. A. No. 1 with maintaining the proper amount of acetone in the autoclave feed.

Nonane boils at 151°C so the separation of nonane and vinyl acetate becomes a simple distillation. The vinyl acetate/water azeotrope make off the column flows to T.A.. No. 1 where the water is separated in a decanter and the vinyl acetate is reused in the autoclave feed. The nonane from the base of the column is reused in the extractors.

The mixture of water, acetone and isopropanol from the extractors, called raffinate, is then (in the case of 13550, 13560 and 13570 columns) fed to the acetone columns and then to the isopropanol column for recovery of these two components. The extractors must be operated so that significant amounts of nonane do not appear in the raffinate. This nonane will end up in the isopropanol

SOLUTION VINYL RESINS PROCESS



ACETONE/ISOPROPANOL RECOVERY
65 AND 80 COLUMNS
BLDG. 114

ACETALDEHYDE REMOVAL
BLDG. 114

UCC
051196

Bldg. 114 - Distillation - continued

causing drying problems at Building 121. The cause of any significant amount of nonane in the raffinate and isopropanol should be determined and corrected. When nonane appears in the isopropanol the Building 121 operators should be immediately notified.

The raffinate from the solvents produced on the "acid" resin (VMCH and VMCC) systems contains a very small fraction of dissolved resin that precipitates in the acetone column causing severe fouling problems. For this reason 13580 column, which was originally an isopropanol recovery column, was converted to a "pre-stripper" so that the recovery of acetone could be conducted in a column free of plugging. The original trays in "80" column were replaced with baffle trays, which while not being very efficient as distillation column trays, are resistant to plugging. In 80 column the acetone and isopropanol pass overhead while the solids and most of the water pass out the base. The overhead goes to 13565 column where the acetone is removed from the head of the column and the isopropanol from the base.

80 column fouling is a serious problem and may be the worse threat the department faces at this time to maintaining smooth, uninterrupted operations. A massive effort is being mounted by R & D and production to find additives and operating techniques that will reduce the plugging frequency of this column. From time to time, various additives will be tried at varying addition rates. Be very attentive to the instructions regarding these additives - the program's importance cannot be overemphasized.

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Bldg. 114 - Distillation - continued

In the solution vinyl resins process one by-product contaminant produced in very low quantities that must be removed and not allowed to accumulate in the system is acetaldehyde. Acetaldehyde has the same general effect as acetone in the autoclaves - it lowers the molecular weight of the resin only it is a much stronger depressant than acetone. The normal concentration of acetaldehyde in the autoclave feed is approximately 500 PPM (0.05%). Anytime this concentration rises to 1000 PPM in the autoclave feed, serious molecular weight problems can be expected and unusual measures should be taken to determine and eliminate the source of the acetaldehyde.

Acetaldehyde is generally produced in the solvents storage and distillation units. Due to its boiling point of 20.9°C it will accumulate in the head of the acetone and vinyl acetate columns. For that reason the make from these columns is "pasteurized", meaning that the make is taken off below the top tray rather than being taken from the condensed overhead. To effectively remove the acetaldehyde which accumulates in the head of the acetone columns the overhead condensate should be kept warm, in the 45-50°C range, so that the aldehyde will be vented off. Each acetone column overhead condenser accumulator is equipped with a vent line to the acetaldehyde removal column (13590). A "heads cut" is also taken off the acetone column overhead condensate and fed to "90" column for aldehyde removal. The feed to 90 column is primarily acetone so the trick here is to separate the aldehyde, which will be flared, and return the acetone to the process. This separation is not particularly difficult due to the wide separation of boiling temperatures between acetone and acetaldehyde, but close attention should be paid to keep 90 column head temperature as specified since an increase in temperature will increase acetone losses and a decrease will cause aldehyde to be returned to the process.

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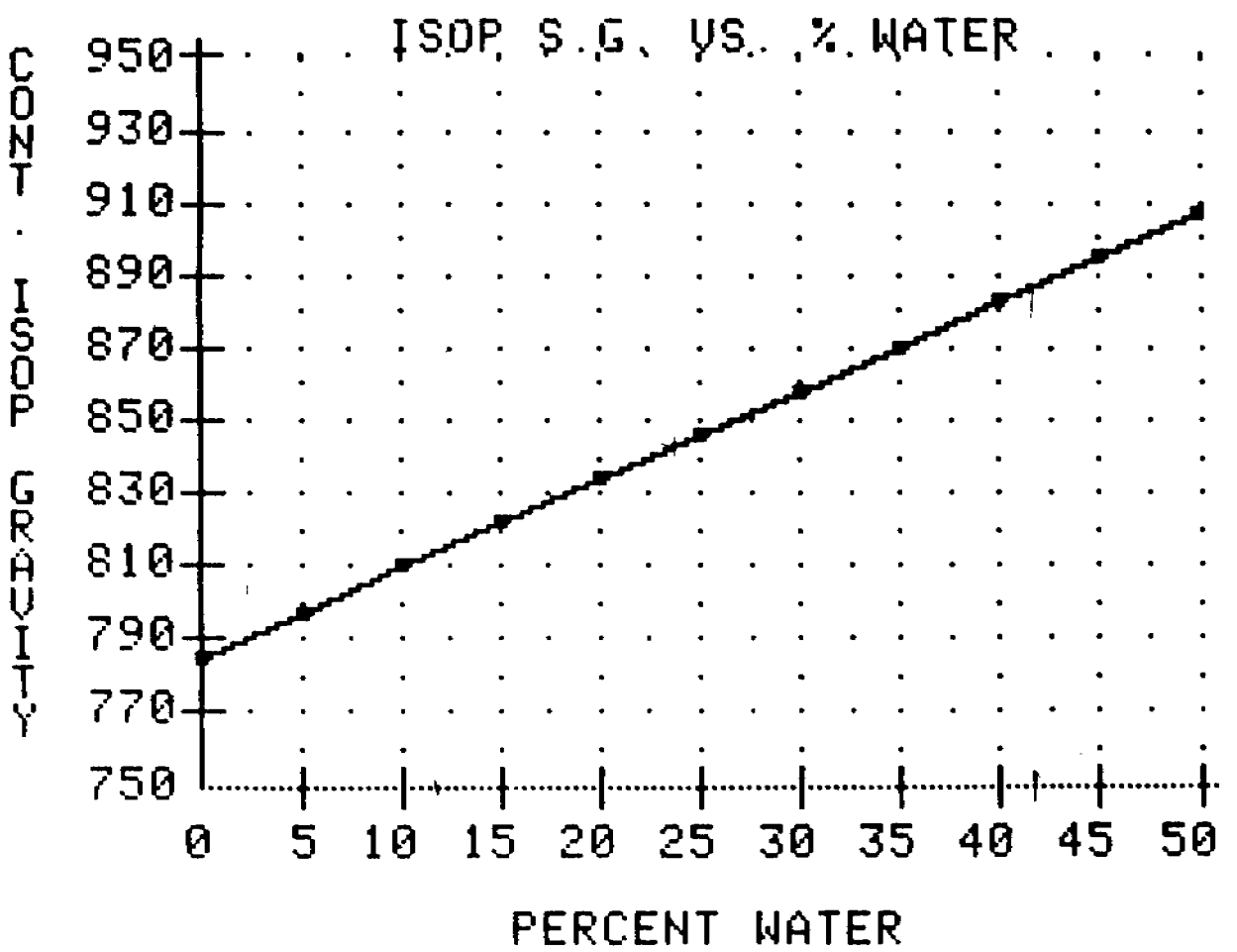
ISOP S.G. VS. % WATER
CONT. ISOP GRAVITY
950
930
910
890
870
850
830
810
790
770
750
0
5
10
15
20
25
30
35
40
45
50
PERCENT WATER

Bldg. 114 - Distillation - continued

The pasteurized make off the acetone columns is a boiling liquid so it is important that the make coolers located in T.A. No. 3 are kept clean on the cooling water (shell) side so that the acetone entering the storage tanks will not be hot, increasing losses through the vents.

The vinyl acetate recovery column overhead condensate should also be kept warm (45-50°C) so that the acetaldehyde will be vented. This vent goes straight to a flare so to prevent loss of vinyl acetate the temperature should not exceed 55°C.

It was brought out in the Building 121 discussion the importance of maintaining the proper isopropanol gravity which is a measure of the contained water. The impregnation operation at Building 121 is particularly sensitive to the water content so it is extremely important that it be held constant. Any significant change in isopropanol gravity should be immediately brought to the attention of the Building 121 operators. The preferred mixture contains approximately 57 percent isopropanol, 35 percent water and 8 percent acetone. This mixture will have a gravity of 0.865. A graph of isopropanol gravity vs water (H_2O) content appears on the next page.

SUMMARY

With the materials recovered in the distillation unit being reused in the process the operation has gone "full circle". From feed preparation, to the autoclaves, to stripping, to precipitation and drying and finally to solvents recovery, the UCAR Solution Vinyl Resin Process is quite a complicated, integrated operation. Unless every facet of this operation is conducted properly and attention is paid to every detail, the whole operation will not function properly. The Building 121 operation is at the complete mercy of the Autoclave, Stripping and Distillation operators. The Autoclave operation is at the mercy of the T.A. No. 1 operator, etc. The Solution Vinyl Resins operation can be an extremely rewarding experience when it is running well. Conversely, when problems are encountered there is probably no more frustrating experience that one can encounter than that of trying to get the operation "back on its feet". Watch the details; ask if you don't know; question if you don't understand. There is no substitute for knowing exactly what is to be done and understanding why it is being done before it is done.

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