POLYVINYL CHLORIDE SUSPENSION RESINS

THE WACKER-CHEMIE PROCESS

REPORT OF PLANT VISIT - NOVEMBER, 1959

UNION CARBIDE PLASTICS COMPANY
DIVISION OF
UNION CARBIDE CORPORATION
SOUTH CHARLESTON, WEST VIRGINIA

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SUMMARY

Wacker-Chemie has two suspension PVC recipes which, when used in conjunction with their process, yield resins which should prove attractive to Union Carbide Plastics Company to manufacture. Currently Wacker is manufacturing both these resins in stainless steel autoclaves of 3,170 gallons and 6,600 gallons capacity using Pfaudler agitation systems. Bakelite, Ltd., has had excellent results using the recipe for one of these resins in its Aycliffe Plant's 3,600 gallon glass-lined Brumagim agitated autoclaves to produce a resin for its hot processing applications. Benefits enumerated for the Wacker technology are good initial color, freedom from fisheyes, high plasticizer absorption with high monomer conversion, and high raw material efficiency. Deficiencies by United States standards are a low apparent density and a broad particle size distribution with a large percentage of fines.

The Wacker recipes use either a low molecular weight methyl cellulose or a polyvinyl alcohol as the suspending medium, with the latter sometimes in combination with an alkane sulfonate as a wetting agent or emulsifier. In addition, salts such as calcium chloride, calcium carbonate, and sodium bicarbonate are incorporated in certain recipes to obtain the desired properties. Dilauroyl peroxide is used as the catalyst.

The Wacker process involves charging water and the miscellaneous ingredients into an autoclave, evacuating the autoclave, charging vinyl chloride, carrying out the reaction, followed by stripping the unreacted monomer from the autoclave, dumping the slurry to a storage tank, running the slurry over a rotary vacuum filter, reslurrying, centrifuging, and then drying in a warm air rotary dryer.

The Aycliffe Plant of Bakelite, Ltd., which is quite similar in process design to the suspension plant in South Charleston, has adopted the Wacker process essentials with a minor capital expenditure. Washing is accomplished by dilution and through the use of wash water in the Bird centrifuges.

It has been recommended that the Development and Production Departments at South Charleston expedite trials of these recipes in plant size autoclaves. Initial efforts should be concentrated on the simpler of the two recipes - one which it is believed can lead to early

relief from our current poor competitive situation. However, slight alterations must be made to the Wacker product to meet the apparent density requirements of our domestic competition.

It is believed that the productivity at Aycliffe can be equalled and improved upon. This would mean a minimum capacity at South Charleston of 38,000,000 pounds per year of first quality resin if the plant were utilized on a single resin basis.

INTRODUCTION

In mid-1959, Union Carbide Plastics Company became interested in reports by Bakelite, Ltd., of the attractive features of the Wacker-Chemie suspension resin process. They had been purchasing a Wacker resin for their hot processing operations and became intrigued by the good characteristics of the resin. After a demonstration in the Aycliffe Plant, Bakelite, Ltd., entered into a licensing agreement with Wacker which permitted Bakelite, Ltd., to adapt the recipe and process technology to their plant at Aycliffe. In addition to having the good hot processing characteristics and freedom from fisheyes as predicted by Bakelite, Ltd., some Wacker resins were found by our laboratories to have excellent initial color and heat stabilities. Another attractive feature of the Wacker technology was the better than 92 per cent vinyl chloride efficiencies reported by Bakelite, Ltd.

As a consequence of these data, Union Carbide Plastics Company entered into an agreement with Wacker-Chemie wherein their polyvinyl chloride recipes and process technology would be made available to Union Carbide Plastics Company, after which a decision would be mad as to whether to produce these products in our suspension facilities. Accordingly, a project team consisting of the three authors visited the Wacker Plant in Burghausen, Upper Bavaria, Germany, from November 16-27, 1959. After this, because the licensing agreement also allow d communication between Union Carbide Plastics Company and Bakelite, Ltd., concerning the Wacker know-how, the project team visited the Bakelite Plant at Aycliffe on November 30-December 2.

This report summarizes information learned during these visits and makes recommendations as to the steps to be taken by Union Carbide Plastics Company.

DISCUSSION

I. Wacker Plant and Process

The plant of Wacker-Chemie at Burghausen, Germany, is a large, integrated plant with facilities for the production of calcium carbide, acetylene, vinyl chloride, and polyvinyl chloride resins. The resins plants are located in the west works of the plant, at a distance of approximately one-half mile from the other production facilities. The resins area was the only portion of the plant which was inspected, and the inspection there was restricted to the building in which suspension vinyl resins are produced. In addition to suspension PVC resins, suspension copolymers, emulsion PVC resins, polyvinyl acetate resins and latices, polyvinyl alcohols, and polyvinyl acetals are produced in the resins area.

The Wacker suspension resins plant capacity is approximately 75 million pounds per year. Some 16 or 17 suspension PVC homopolymer resins are produced. Copolymers are usually produced in an adjacent department. All of the equipment is located indoors in large buildings of masonry construction. The major equipment consists of thirteen 3,170 gallon autoclaves, eleven 6,600 gallon autoclaves, twelve slurry storage tanks, six rotary vacuum filters, four continuous centrifuges, and four warm air rotary dryers. The facilities are arranged in a flexible manner that will permit simultaneous production of up to four products. These production facilities are described in detail below in separate sections discussing the feed preparation system, the reaction system, the monomer recovery system, the recovery system, and the drying system. Another section, "Material Usage", discusses Wacker's vinyl chloride efficiency and utility usages. A final section outlines the manpower employed in the department. A flow diagram of the polymerization and monomer system of a plant designed to use the Wacker technology is included at the end of this report.

A. Feed Preparation System

Most of the vinyl chloride used at Burghausen is produc d by Wacker. Some vinyl chloride is purchased from other plants in Germany and also from plants in Italy. The vinyl chloride for the resins area is stored in eighteen 20,000 gallon horizontal

steel tanks having a design pressure of approximately 100 psig. This represents a total storage volume of approximately five days production. The vinyl chloride is continually circulated between the tanks for blending purposes and thus obtains consistent monomer quality. Details of the storage facilities are shown in the bottom right hand corner of the flow diagram.

The vinyl chloride storage tanks are located at a distance of about 200 to 300 feet from the suspension resins plant itself. The tanks are placed above the normal plant grade and are covered to a depth of three or four feet with earth. A concrete retaining wall at each end of the tanks holds this earth in plac . The earth at the sides of the tanks is sloped at about a 45 degree angle. The vinyl chloride is circulated with horizontal turbine pumps and is filtered as it is circulated in order to remove any solid particles. The vinyl chloride storage tanks are emptied and cleaned once a year.

The vinyl chloride is transferred from the field storage tanks into a 1,300 gallon storage tank located inside the building. The vinyl chloride is then pumped from the tank with a horizontal turbine pump through a positive displacement meter to a header feeding the autoclaves. A 40-mesh filter is located ahead of the vinyl chloride meter. Recovered vinyl chloride is stored in a separate tank and is blended into the autoclave charges. Line filters are provided immediately before the vinyl chloride pump and also immediately before the positive displacement meter. The vinyl chloride header serving the autoclaves is dead-ended and is not self-draining.

The process water used in the Wacker suspension resins unit is deionized water, having a conductivity of 0.1 micro-ohm-centimeters. The deionized water is prepared at a central location in the main plant and this system was not inspected. It was reported that the raw material was treated with a flocculent and then settled in basins. The clean water is then deionized in a mixed bed exchange unit. This arrangement is similar to that at South Charleston.

The deionized water for reslurry and washing operations is used directly as received. This water is transferred in rubber-lined steel pipe. The deionized water used in the reaction system is deaerated in a vacuum system as illustrated in the

upper right-hand corner of the flow diagram. In this system the fresh water is heated in a heat exchanger with steam and water flows down over a disc and doughnut type degasser. This degasser is maintained at 150 mm pressure by a rotary vacuum pump. A condenser is provided in the vent line to separate water from the exit gas. From the degasser, the water flows by gravity to an 8,000 gallon rubber-lined storage tank. From this tank the hot water of 50 to 60°C is pumped through filters to a header supplying the polymerization autoclaves. A positive displacement meter is provided in this pipeline to meter the water charged to the autoclaves.

The suspending agents and the emulsifiers are dissolved in a 1,500 gallon mixing tank and are then centrifuged in a disc-type centrifuge to remove insoluble material. The centrifuge is used in preference to a filter because it will remove some gel particles which deform and pass through filters. Four agitated tanks are provided for solution storage. Quantities of these solutions are weighed into containers for the individual autoclave charges. The calcium chloride, calcium carbonate, sodium carbonate, and dilauroyl peroxide are added directly to the autoclaves without prior mixing.

B. Reaction System

The detailed recipes and a detailed description of the reaction cycle are presented in the section of the report entitled "Polymerization Procedures". Briefly, the clean autoclaves are charged with the proper quantity of hot deionized water through a rubber hose inserted in the open manhole. The other dry ingredients are added through this opening and the solutions of suspending agent and emulsifier are pumped into the opening from a small tank mounted on a four-wheel cart. The manhead is then replaced, the autoclave evacuated, and the vinyl chloride pumped into the autoclave. The reaction proceeds in a period of 16 to 32 hours, depending upon the recipe and the type of resin. Upon completion of the reaction, the vinyl chloride vapor is stripped from the autoclave. The manhead is then opened, and the autoclave is dumped into slurry storage tanks located below. Loose resin on the walls is washed from the autoclave into the storage tank with deionized water. The autoclaves are then cleaned by laborers who enter the autoclave.

The autoclaves are equipped with a circulating water system. The water is pumped in a 222 gallon per minute centrigugal pump into the bottom of the autoclave jacket. The water overflows from the top of the jacket into a standpipe on the pump suction. The cooling water temperature on the autoclave jacket is controlled in order to control the reaction temperature. The controllers admit steam or cooling water as required to adjust the temperature. The heads of some of the Wacker autoclaves are jacketed and cooling water can be added to the jacket on the head through a separate connection with the cooling water header. This water is apparently used only in emergencies. The autoclave jackets are said to have spiral baffles. The normal usage of fresh water is 53 to 68 gallons per minute. Excess water overflows from the standpipe to a water-return header operating at atmospheric pressure.

All but two of Wacker's 24 autoclaves are of stainless steel construction in two sizes: 12,000 liters (3,170 gallons) and 25,000 liters (6,600 gallons) nominal capacity. The two different autoclaves are standard Pfaudler-designed, glass-lined vessels of 16,000 liter capacity (4,225 gallons). Two types of agitators are used in the autoclaves. The first is considered obsolete and consists of a flat plate mounted axially on a vertical shaft. These are used without baffles and run at 60 rpm. The second type is a standard 120 rpm Pfaudler, three blade, retreating blade impeller used with a regular Pfaudler finger-type baffle. These are made of stainless steel and are not glass coated. The older, less effective, single-speed plate stirrers are being progressively replaced by the Pfaudler systems. Both types of agitation and both stainless and glass autoclaves are used more or less interchangeably for the same kinds of resin production, although some modification of recipe is sometimes used to compensate for the more effective Pfaudler agitation, as experience indicates may be necessary. A schedule of autoclave arrangement is included below.

Number	Size	Material	Agitation
6	6,,600 Gallons	Stainless Steel	Paddle
3	3,170 Gallons	Stainless Steel	Paddle
9	3,170 Gallons	Stainless Steel	Pfaudler
2	4,225 Gallons	Glass-Lined	Pfaudler
3	6,600 Gallons	Stainless Steel	Pfaudler
1	3,170 Gallons	Stainless Steel	Paddle Plus Auxiliary 8 Inch Turbine

One of the Wacker autoclaves having a large paddle agitator has a supplementary high speed turbine wheel located above and to one side of the main paddle. This turbine operates at a speed of 900 rpm and has a wheel about eight inches in diameter. Patent application has been made for this peculiar agitation system.

C. Monomer Recovery System

The vinyl chloride vapor is removed from the autoclave through an electrically driven reciprocating compressor. A 1,320 gallon foam trap is located between the autoclaves and the compressors. This foam tank is on a weigh scale. The balance arm of this scale is observed during the stripping operation to determine if foaming is occurring. Two electrically-driven, horizontal, single-cylinder, double-acting compressors are provided. Either of these is capable of compressing the strippings from the autoclave in about 30 minutes. These compressors are cross-connected to permit either compressor to be used on any of the autoclaves. The vapor to the compressor is filtered. A safety valve discharging out of the building is provided on each compressor discharge line. These were the only safety valves seen in the plant. The compressed vinyl chloride vapor at about 60 psig flows to two condensers (each 400 square feet estimated) in parallel with river water in series flow through the two condensers. On the water side the condensers have a single vertical baffle. The condensed vinyl chloride flows by gravity to a 1,320 gallon weigh tank. A duplicate set of two condensers is provided. The second set is used when the first set is shutdown for cleaning. This is required onc every four months because of the buildup of polyvinyl chloride polymer inside the tubes. The condensed, recovered vinyl chloride is pumped from the weigh tank into the autoclaves where it is blended with fresh vinyl chloride.

In addition to the regular vinyl chloride stripping line, two separate emergency vent headers are provided for blowing down autoclaves in the event of a runaway reaction. No safety valves are provided on the autoclaves. Each autoclave is equipped with a pressure recorder and two separate and independent pressure gauges.

The recovered vinyl chloride tanks, the autoclaves, and the associated piping are constructed of stainless steel, German normale-N-45/41, which is a steel containing 17 to 19 per cent chromium, 9 to 11 per cent nickel, with traces of titanium. The maximum carbon content is 0.12 per cent.

D. Resin Recovery System

Upon completion of the reaction, the slurry is dumped from the autoclaves into one or more of twelve 4,360 gallon open-top slurry storage tanks which are located on the floor level below the autoclaves. Portable four inch diameter aluminum pipe is provided to permit the operators to pipe up any autoclave to any storage tank. These lines are frequently rearranged and eliminate the need for expensive valve and pipe arrangements. The aluminum pipe has a ball and socket joint with an external clamp. The 12 slurry storage tanks are agitated with a paddle-type agitator rotating at 20 rpm. The slurry contains approximately 30 per cent total solids when dumped from the autoclave.

The slurry is pumped with a centrifugal pump into the pan of a rotary vacuum filter. These filters have six troughs f r adding wash water to the filter cake. In addition, the centrifuge effluent is returned to the pan of the rotary filter. The filter cake is dumped directly into a reslurry tank in which enough fresh deionized water is added to reconstitut a slurry containing 30 per cent total solids. The filter cake varies between 50 and 65 per cent total solids depending upon the fineness of resin particles produced in the different products. For some products, this reslurried resin is pumped to centrifuges located in the drying area of the building. For other resins, the reslurried material is filtered, washed, and reslurried again before being pumped to the centrifuges.

For a few resin types, the slurry is passed to a mill in which the resin is ground in order to reduce particle size. This ground resin is then recovered on a filter and reslurried in the conventional manner. The slurries are handled in either aluminum pipelines or stainless steel pipelines.

The rotary vacuum filters have a drum diameter of about 48 inches and are 15 inches wide. The filter drums have manually adjustable speed and operate at about 2 rpm. The filter

area is about 20 square feet. The filter cake thickness is about 1.25 inches and the capacity per filter is approximately 4,500 pounds per hour.

Vacuum for the filters is provided by a Nash-Hytor type vacuum pump which removes the air from a small tank which is elevated in order to provide a 30-foot barometric leg. The mixture of water and air flows up to this tank where the water and air are disengaged. The water then flows by gravity to a 2,100 gallon settling tank located in the basement of the building. Any resin which inadvertently passes the filter (for example, from a break in the filter cloth) settles in this tank. Second quality resin is recovered from this tank approximately every four months. The water from the settling tank overflows into a second settling tank of the same size from which water containing about 40 grams of resin per cubic meter flows into the sewer system.

The total water consumption, averaged for all resins, is eight pounds per pound of resin. This is distributed roughly as follows:

Autoclave Charge	2.3 Pounds
Wash Water	1.0 Pounds
Reslurry Water	1.3 Pounds
Second Wash	1.0 Pounds
Second Reslurry	1.3 Pounds

The balance of the water consumption represents water wastage.

E. Drying System

The reslurried resin from the recovery system is pump d through a circulating line to the centrifuges located on th sixth floor of the drying building. The slurry flows into a two gallon constant head tank with a glass shell. The over-flow from the tank returns to the reslurry tank by gravity. A side stream flows from the constant head tank down t the centrifuge through a sight glass. The flow of slurry to the centrifuge is regulated by a manual control valve. A c ntrol valve provides automatic closure in the event of failure in power to the centrifuge.

The Wacker centrifuges are of the horizontal oscillating type manufactured by a Swiss firm. The effluent liquid from the centrifuges contains from one to five per cent total solids and is recycled to the rotary filters in the recovery system. The cake is discharged from the centrifuge at 60 to 70 per cent total solids and drops by gravity into the rotary dryers. An internal pipe guides the resin through a stationary end section and discharges the resin into the rotating barrel of the dryer.

Two of the rotary dryers are of stainless steel and two are of aluminum. The dryers are six to seven feet in diameter by about 35 feet in length. The dryers have a complicated system of complex internal longitudinal baffles. These baffles leave a maximum free space for the fall of resin of about 18 inches. A 150 mesh screen is provided between the air heaters and the rotary drum.

Heat for the drying operation is supplied by hot air. The air enters a treating room in the building through louvers. It is then preheated with vertical finned tube steam heaters. The preheated air is first filtered on two oil bath filters approximately 8 feet by 10 feet in size which is followed by a cloth filter. A 24 inch diameter air duct conveys the filtered air from the room to the blower. This blower forces the air through a heater in which the air is heated to 150 to 160°C. The heated air then flows through the dryer, emerging at a temperature of 60°C.

Each of the four dryers has a resin drying capacity of 2,000 pounds per hour. The air rate is said to be 14,700 cubic feet per minute. The resin from the end of the dryer barrel drops into a discharge hopper in which the air and resin are separated. The air from the hopper flows to a cyclone separator which is four feet in diameter. The separator has a long tapered conical section about ten feet long and a straight section of about six feet. The inlet dimensions of the separator are about 10 inch s by 36 inches and the inlet velocity is approximately 100 feet per second. The outlet duct is about 24 inches in diamet r. A separation efficiency of 99.3 per cent is claimed for this separator.

The pressures through the drying system are as follows:

Suction of Blower at Dryer Inlet	-0.3 Inches, Water
Dryer Inlet	+1.0 Inches, 150-160°C
Dryer Outlet	Atmospheric
Centrifugal Separator Outlet	-4.3 Inches
Baghouse Outlet	-5.5 Inches, -14 cm.
Exhausting Blower Discharge	+0.8 Inches, +2 cm., 60°C

The resin drops from the dryer discharge hopper and from the cyclone into a vibrating four mesh screen which removes coarse material as off-grade resin. The screened product goes to the inlet duct of a 30 inch diameter, 50 horsepower blower which blows the resin up to a cyclone separator above the Niagara type sieves on the sixth level.

The outlet air from both cyclones flows to a baghouse having a cotton bag area of 1,720 square feet. The baghouse pressure drop is about one inch of water. The recovered resin is either returned to the discharge hopper on the dryer or alternatively is bagged as second quality resin. A blower on the baghouse outlet exhausts the air to the atmosphere above the top of the building.

The dried resin is screened in vibrating sieve machines which are similar to the Niagara Super-Sifter. Nylon screens are arranged 12 high in 2 stacks as follows:

1,000 Micron	2
150 Microm	8
200 Micron	2

The last screen size is included as a guard feature to prevent serious resin contamination in the event of 150 micron screen breakage. The sieves are equipped with rubber balls to keep the screen openings clear. Wacker is currently experimenting with polyvinyl chloride balls as a substitute for the rubber balls.

The resin from the sieves drops into 3,000 cubic foot intermediate storage bins. These bins are concrete silos painted on the inside with polyvinyl acetate paint. The Wacker representative stated that this paint is very satisfactory. The resin is transferred and blended from the intermediate storage bins into product storage bins which have a capacity of 21,000 cubic feet. These bins are also constructed of vinyl painted concrete.

The product is bagged from the final storage bins at eight bagging stations. The bagging operation is entirely manual and the material handling is largely manual. At the time of observation two bagging stations were being operated by four men. In addition, five men were employed in moving the bags to box cars on an adjacent railroad siding. This combination was loading about one 77 pound bag per minute at each station.

In an effort to provide the increased drying capacity required to dry the recently developed porous resins, one drying system has been equipped with a first-stage flash dryer. This flash drying system is of conventional design. The partially dried resin from the flash dryer drops into a rotary dryer similar to the one which has been described.

F. Material Usage

The vinyl chloride consumption per pound of polyvinyl chloride suspension resin has been improving from year to year. The following annual averages were supplied by Wacker:

Year	Pounds Vinyl Chloride Per Pound Resin
1957	1.099
1958	1.080
1959	1.070 to 1.080

The above numbers include second quality or scrap resin amounting in 1958 to 1.88 per cent of total resin production.

Present utility usages per pound of resin are summarized below:

Deionized Water	8 Pounds Per Pound Resin
Cooling Water	15.6 Gallons Per Pound Resin
Steam	2 Pounds Per Pound Resin
Brine	0
Nitrogen	0

G. Operating Personnel

The entire operation falls under the supervision of one person who is responsible for the development, quality control, and production of these resins. He has three principal assistants in the plant area: one in the control section, one chemical engineer to supervise plant operations, and one "master" foreman who is responsible for all shift personnel and their operations.

The shift operating force consists of 17 men as follows:

Foreman
Charging Operator
Stripping Operator
Autoclave Operator
Filter Operator
Dryer Operator
Mill Operator
Pumper
Autoclave Cleaners (3)
Baggers (5)
Laboratory Analyst

Additional day personnel staff the control laboratory, make suspending agent solutions, repair work, etc.

II. Wacker Recipes and Technology

A. Recipes and Resin Properties

A brief explanation of the resin codes used by Wacker will help provide a better understanding of their recipes and technology. They have two basic suspension recipe systems: one which uses a suspending colloid only and is designated by code letters "HH" and another which uses a combination of a suspending colloid and a wetting agent or detergent and is designated by a single code letter "H". A typical example of the first system is HH 100/60, of the second H 100/60. The number "100" refers to a 100 per cent polyvinyl chloride resin; the number "60" represents the Fikentscher K-value, a measure of resin molecular weight. The relation between K-value and specific viscosity is shown in Figure 1. The details of specific recipes and their resulting resins are presented with a supplement in Table I for summation and reference.

Wacker produces suspension polyvinyl chloride resins chiefly by four different recipes: two of the HH-type and two of the H-type. Their major resin designations are:

1. HH 100/KD) Same recipe and polymerization technique.
) The D-type resins are wet milled to pro-
2. HH 100/K) duce HH 100/K.

3. HH 100/Kf

4. H 100N/K

5. H 100/K

The K-values of any of these recipes may be 60 to 80, depending upon specifications for customer requirements. The most common values are 60, 65, 70, and 75, corresponding to specific viscosity values of 0.162, 0.189, 0.219, and 0.252 (see Figure 1). These molecular weight levels, coupl d with the particular resin characteristics from each recipe, appear to satisfy the European market for hot processing resins for calendering, flooring, and extrusion applications. There is little or no demand for dry-blending type resins and Wacker has no particular interest in such resins, although the HH/100KD type resins described below are marginal in dry-blending properties. Less than five per cent of Wacker's total sales is in this latter resin.

TABLE I

WACKER CHEMIE RECIPES AND RESIN CHARACTERISTICS

K-VALUES OF 60 TO 80 (SPEC. VISC. OF 0.155 TO 0.275)

RESIN TYPE

Recipe Components (1)	HH 100/KD (2)	HH 100/K	HH 100/Kf (3)	H 100N/K (4)	H 100/K
Suspending Agent	POLYVIOL W25 VZ100 (5) 0.04-0.05%		METHOCEL 10 (6) 0.09%	POLYVIOL W25 VZ190 0.25%	POLYVIOL W25 VZ190 0.50%
Emulsifie.	None	This resin is polymerized by same recipe and procedure as HH 100/KD - it is wet-milled to reduce particle size	None	NEKAL BX (7) 0.25	MERSOLAT K (8) 0.12
Calcium Chloride	None		None	0.09	0.12
Sodium Bicarbonate	0.003		0.11	0.015	None
Calcium Carbonate	None		None	0.03	0.012
Dilauroyl Peroxide Catalyst	Varies with temperature of polymerization, for K = 70, T = 59°C, catalyst concentration = 0.062%				
Lauric Acid	None	None	None	None	0.3 (9)
Dichloroethylene	Used only for K-value $\leq$ 60, as mol. wt. degrader to keep within 150 psig pressure limit of autoclave				
Monomer/Water, by wt.	37/63	37/63	38/62	30/70	H 100/60 - 25/75 H 100/70 - 31/69 H 100/80 - 30/70
pH Range of Water Solution	4.0-4.5	4.0-4.5	7.5-8.5	7.5-8.0	5.6-6.5
Conversion, %	70 to 80, termin. on a time basis	"	70 to 80, termin. at 16 hrs.	90, 40 psig drop	90, 40 psig drop
Autoclave Sizes	12,000 liter (3170 gal.) or 25,000 liter (6600 gal.) stainless steel				
Washing and Filtration Cycles	Once	Once	Once	Twice	Twice
Agitation	Standard Pfaudler system at 100 rpm or rotating plate type at 50-60 rpm with no baffles				
Resin Properties					
Particle Size - % thru 100 micron screen	25-50	80-95	70-90	80-95	80-95
Apparent Density (Shaken)	31-37 lb./cu. ft.	29-31 lb./cu. ft.	26-30 lb./cu. ft.	No data	20-24 lb./cu. ft.
Plasticiser Acceptance	Poor, 50%	Best, 100%	Good, 90%	Good, 80%	Good, 90%
Initial Color	Best	Best	Fair	Poor	Poor
Ultimate Stability	Poor	Poor	Fair	Best	Best
Electricals	Best	Best	Best	Poor-not acceptable	Fair

NOTES

(1) Based on vinyl chloride.

(2) "D" indicates resin for dry-blending applications.

(3) "f" indicates a fine product, as polymerized.

(4) "N" has significance only to Wacker (possibly refers to NEKAL BX).

(5) *POLYVIOL* is Wacker's partially hydrolysed polyvinyl acetate. *See* Table VI for comparison to American materials.

(6) METHOCEL 10, from Dow Chemical Company. A German methylcellulose, CULMINAL, can be substituted, but only 0.015% sodium bicarbonate is then used because CULMINAL contains more salts than METHOCEL.

(7) NEKAL BX is diisopropyl naphthalene sulfonate.

(8) MERSOLAT K is a secondary alkyl sodium sulfonate (from a C_{12}-C_{16} straight chain Fischer-Tropsch by-product).

(9) Lauric acid used only for resin for certain customers who require good color stability with certain types of light stabilizers.

From the list of resins included in Table I, Wacker is promoting two types, HH 100/Kf and H 100/K, and trying gradually to eliminate the others from their production. These two preferred resins are characterized by low to intermediate apparent densities; good plasticizer absorption; and acceptable heat stability, initial color, and electrical properties for many applications. Production economy is also recognized for these products since the H 100/K recipe goes to 90 per cent conversion and neither recipe requires the additional step of wet-milling of the resin to reduce particle size or improve plasticizer acceptance.

To further indicate Wacker's reasoning for this selection, the resins being displaced have several disadvantages. The HH 100/K series requires wet-milling to break up agglomerates and increase porosity and there is a very limited market for the unmilled version, HH 100/KD. The H 100N/K series uses a napthalene sulfonate type detergent, Nekal BX, which spoils the electrical properties of the resin, even with resin washing, and also lowers the initial color rating of the material with some stabilizers. In view of these differences, we believe the Wacker promotion scheme has merit also for our purposes and we have concentrated chiefly on the techn logy for producing HH 100/KF and H 100/K type resins.

Both of these resins have excellent properties for hot processing applications. Apparent densities are generally low (less than 30 pounds per cubic foot), particle sizes are fine (55 to 70 per cent by weight is smaller than 100 microns), and plasticizer acceptance at room temperature is high (50 to 70 per cent).

The two selected recipes also showed possible advantages for initial color in compounds, which is a subject of prime importance to the Corporation at this time. Sufficient compounding materials from our laboratory were taken to the Wacker Plant to make several evaluations for initial color by our Press Plaque "C" heat stability test* in their lab ratory on current production resins. The resin type HH 100/65f, produced by the Methocel recipe, whether washed or not during recovery in production equipment, exhibited an initial color better than a competitive resin, Marvinol VR-24,

*D-3346-125, Tentative Method for Thermal Stability

currently acceptable to Elm Coated Fabrics Company. The other resin, H 100/65, made with Polyviol and Mersolat, had initial color equivalent to the VR-24 after the two standard production washing cycles. However, the initial color of this resin, as recovered directly from the autoclave slurry without washing, was inferior to both VR-24 and the washed resin. These comparisons are important in adapting recipes to our present plant in view of the present lack of equivalent facilities for washing resins during recovery as provided by the Wacker process.

Although no comparative data are available, observation of quality control laboratory operations periodically during our visit indicated that these resins are very low in fisheyes or hard resin particles and they can be rapidly hot processed to provide high quality film and sheeting products. This impression was gained from observing two evaluations, the Mill Stability test at 150°C and a Brabender Plastograph test, both of which will be described later.

The suitability of these resins as produced by Wacker for markets in the United States has been summarized by Mr. D. L. Engle in a recent memorandum.* The conclusions made in this memorandum on samples of resin evaluated prior to our inspection trip require no revision. Our experience has not provided any reason to reject the views expressed: (1) that the Wacker resins have adequate thermal stability for most domestic calendering applications, and (2) that the particle geometry requires adjustment (to larger particle size, higher apparent density, and/or lower plasticizer absorption) before these resins could be considered interchangeable with Marvinal VR-24, VR-23, Geon 103EP, Escambia 2185, and Presto P-325 which are used by major accounts of interest to the Corporation.

B. Polymerization Procedures

1. Autoclave Preparation

At Wacker, each autoclave is manually cleaned of ivory and scale after each run. Following dumping, rinsing, and ventilating after a previous run, one man can

*D. L. Engle, Wacker-Chemie Vinyl Resins, Current Estimate of Market Acceptance, Development Department Project 510B, File No. B:01:500-M13, September 15, 1959.

usually scrape clean the walls and agitator in less than one hour because the surfaces are very smooth and one run does not result in excessive fouling. After the manual cleaning, the autoclave is rinsed, the bottom dump valve closed, and the manhead left open. No pressure test is made prior to charging for the next run.

2. Autoclave Charging and Operation

The following stepwise procedure is followed for all types of suspension polyvinyl chloride resins produced at this plant. Attached Tables II and III (pages 23 and 24) list the operating instructions posted for the HH 100/70F and H 100/60 resins.

a. Water - The required weight of preheated (50-55°C), deaerated, ion-exchanged water is pumped through a calibrated meter into the autoclave manhead from a short length of hose on the header.

b. Suspending and Wetting Agents - Prepared solutions of the required materials are weighed from storage tanks into aluminum weigh tanks mounted on pump carts designated for the particular solutions desired. The pump carts are then pushed to the autoclave and the solutions pumped in through the open manhead. This eliminates the use of large pumps and headers which tend to become fouled with gels and cause cross-contamination of these carefully prepared solutions when different charges are required for the different recipes. The Wacker people feel that elimination of all insolubles and gels from these solutions is necessary for preventing fisheyes in the resin. The preparation of the solutions will be described later.

c. Salts for Suspending Action and Buffering - Preweighed polyethylene bags of the required salts are emptied into the charge through the manhead and the agitator turned on for two to three minutes to mix the water soluble components.

d. Charge Control Sample - A sample of the aqueous solution in the autoclave is dipped out and sent to the control laboratory for a "drop-count" test, to be described later. This is a reference sample to monitor the critical charge components. Completion of the charge is not delayed for results of this test.

e. Catalyst and Autoclave Closing - Preweighed polyethylene bags of dilauroyl peroxide are emptied through the open manhead. After this addition the autoclave is closed and fitters remove slip blanks and replace flanged sections in the monomer feed line and monomer stripping line to the autoclav .

f. Autoclave Evacuation - With the agitator stopped, the autoclave is opened to a vacuum header and evacuated to a final pressure of 100 mm for 30 minutes. During this time, no appreciable foaming of the charges was observed and the solutions did not boil. Observation of a vacuum recorder chart is relied upon to show any excessive leakage into the autoclave. Should the pressure not drop as desired, connections are tightened until the vacuum chart shows the desired readings. The vacuum for this step was provided by a Nash-Hytor type pump which vented to the air. There was no connection between this evacuation system and the vinyl chloride stripping and recovery system.

g. Vinyl Chloride - The vacuum is broken by the metering of the required amount of vinyl chloride through a rotary positive displacement meter. Pressure for charging the monomer is provided by a six stage turbine pump. No nitrogen or oth r inert gases are utilized in the monomer systems. Various proportions of recovered and fresh monom r are used, but only up to 50 per cent recovered monomer is used for any one charge.

h. Polymerization - The agitator is started during the monomer addition and the temperature control s t for the desired operating level for the K-value

desired. Operating time is determined by the type of recipe and resin. Some recipes are terminated at 16 hours or about 70-75 per cent conversion, others are stopped at the beginning of pressure drop, and still others are stopped after a pressure drop of approximately 40 psig. Because of the range of temperatures used for the range of K-values desired, the operating times vary in this respect also. For example, a run of HH 100/75f (η_{sp} = 0.252) is made at 45.5°C for 29 hours with a conversion of approximately 70-75 per cent. A run of H 100/60 (η_{sp} = 0.162) is made at 59°C and goes to pressure drop in 15 hours for a conversion of approximately 85 per cent. There is little compensation of catalyst concentration for the different temperatures, 0.1 per cent dilauroyl peroxide for the longer run, 0.08 per cent for the shorter, which explains the differences in polymerization times.

i. Special Additives - In the preparation of resins with a K-value of 60 or less, with the limit of autoclave pressure of 150 psig, a mixture of C15 cis-trans dichloroethylene is used as a degrader. In the charging scheme, this material is pumped into the autoclave from a weigh tank after evacuation but before vinyl chloride addition. For certain H 100/60 resins, lauric acid is added through the open manhead before the sample for the laboratory is taken.

j. Termination - With the agitator and autoclave temperature maintained, termination of a run is started by stripping the unpolymerized vinyl chloride to the monomer recovery system. Stripping is aided by the compressor in the system and the autoclave pressure is reduced to approximately atmospheric before the stripping system is closed off and the autoclave manhead opened. Stripping times vary from thirty minutes to over five hours, depending on the recipe and degree of conversion.

k. Resin Slurry Sampling - After the manhead is removed, the operator dips out a small slurry sample and takes it to the control laboratory for a microscope viewing.

If, in the opinion of both the operator and laboratory analyst, the particular sample appears representative of the type of resin desired, notation is made in the record book and the material classified first or second grade. First grade resin is sent through a conventional filtration, washing, centrifuging, and drying sequence. Second grade resin is pumped to large vats for collection until enough has accumulated to warrant a recovery operation.

3. Preparation of Suspending and Wetting Agent Solutions

As mentioned previously, the Wacker process provid s particular techniques for making clean solutions of the various suspending and wetting agents. The technique for all the materials is essentially the same except for the different concentrations as required to provide the needed product characteristics. The Methocel and Polyviol (polyvinyl alcohol) solutions were made at five per cent concentrations, the Nekal BX at seven per cent, and Mersolat at 30 per cent. In a separate glass-lined agitated 1,500 gallon tank, the required amount of agent is dissolved in heated water. In transferring this solution to a storage tank, the solution is first run through a cl th filter to remove gross insolubles and dirt, then centrifuged for clarification and gel removal in a DeLavel totally enclosed continuous centrifuge. The ready-to-use solutions are stored in stainless steel tanks and sampled periodically for solution total solids to provide uniformity of charging. Polyviol solutions are normally used within a day or so of preparation, but solutions would not be stored for more than two to three weeks because of changes in the suspending ability, particularly in the case of Polyviol. Since the tanks are indoors, no heating or steam tracing is necessary to protect the solutions or lines from freezing.

C. Control Tests at Wacker

In the appendix are listed the various control tests performed on the raw materials used in the polymerization recipes and on the products of these recipes. Certain tests are discuss d in some detail and the results interpreted. It is planned to issue a supplemental report detailing certain test methods that may be of value in the Plastics Company's operations.

TABLE II

WACKER AUTOCLAVE CHARGES AND INSTRUCTIONS
AS ISSUED FOR HH 100/70f RESIN

Item	Charge Proportions	Charge for Autoclaves, Kilograms (Pounds)			
Autoclave Number		12*	8	20	21
Autoclave Capacity		12,000 Liters (3,170 Gallons)	12,000 Liters	16,000 Liters (4,230 Gallons)	25,000 Liters (6,600 Gallons)
Autoclave Construction		Stainless Steel	Stainless Steel	Glass	Stainless Steel
Autoclave Agitation		Pfaudler	Pfaudler	Pfaudler	Pfaudler
(1) Demineralized Water	62 Parts	6,500 (14,300)	6,500 (14,300)	7,500 (16,500)	13,500 (29,700)
(2) Start Agitation	-	-	-	-	-
(3) Methocel 10 Solution - 5%	0.09%**	-	70 (154)	85 (187)	140 (308)
Culminal Solution - 5%	0.09%	70 (154)	-	-	-
(4) Sodium Bicarbonate	0.11% or 0.015%	0.6 (1.3)	4.5 (9.9)	5.0 (11.0)	9.0 (19.8)
(5) Sample for Control Lab	-	-	-	-	-
(6) Dilauroyl Peroxide	0.062%	2.5 (5.5)	2.5 (5.5)	2.8 (6.2)	4.5 (9.9)
(7) Evacuate 30 Minutes, No Agitation	-	-	-	-	-
(8) Vinyl Chloride	38 Parts	4,000 (8,800)	4,000 (8,800)	4,500 (9,900)	8,000 (17,600)

Temperature 53.5 - 54.0°C
Reaction Time 16 Hours

*With the use of Culminal (a German type of methylcellulose, 10 cps viscosity), only 0.015 per cent bicarbonate was required because of the higher salt content of Culminal compared to Methocel 10.

**Per cent based on vinyl chloride.

TABLE III

WACKER AUTOCLAVE CHARGES AND INSTRUCTIONS
AS ISSUED FOR H 100/60 RESIN

Item	Charge for Autoclaves, Kilograms (Pounds)	
Autoclave Number	1	2
Autoclave Capacity	12,000 Liters (3,170 Gallons)	25,000 Liters (6,600 Gallons)
Autoclave Construction	Stainless Steel	Stainless Steel
Autoclave Agitation	Plate	Plate
(1) Demineralized Water	7,300 (16,050)	15,000 (33,000)
(2) Start Agitation	-	-
(3) Mersolat Solution, 30%	10 (22)	24 (53)
(4) Polyviol V 190, 5%	245 (539)	600 (1,320)
(5) Calcium Chloride, Hydrated	3.0 (6.6)	6.6 (14.5)
(6) Calcium Carbonate	0.3 (0.7)	0.66 (1.5)
(7) Lauric Acid	7.5 (16.5)	15 (33)
(8) Sample for Control Lab	-	-
(9) Dilauroyl Peroxide	2.0 (4.4)	4.0 (8.8)
(10) Evacuate 30 Minutes, No Agitation	-	-
(11) Cis-Trans Dichloroethylene	30 (66)	66 (145)
(12) Vinyl Chloride	2,500 (5,500)	5,500 (12,100)

Temperature 59°C

Reaction stopped by starting stripping at start of pressure drop, approximately 15 hours.

Screened on 150 m (100 mesh) screens after drying. Oversize is milled and rescreened.

III. Adoption of the Bakelite, Ltd., Aycliffe Plant to the Wacker Process

The project team visited the Bakelite, Ltd., suspension resin plant at Aycliffe from November 30 through December 2, 1959. This plant has been producing suspension resins for about three years and was designed to conform with Union Carbide Plastics Company's suspension resin process. Thus, as it had been operated, it was very similar to the Suspension Unit at South Charleston with autoclaves, blowdown tank, hot wet stripping tanks, Bird centrifuges, and flash dryers.

For the past six months, however, this plant has been using the Wacker recipe for the H 100/K series of resins and has been employing several of the Wacker process techniques. All, or almost all, of the Aycliffe product is hot processed. The plant personnel consider the Wacker recipe product, designated DVY-11 by Bakelite, Ltd., to be an excellent hot processing resin with remarkable freedom from fisheyes. In addition, the Wacker techniques have allowed Aycliffe to attain vinyl chloride efficiencies in excess of 93 per cent on gross resin production.

A. Recipe

When Bakelite, Ltd., first became interested in the possibility of producing the Wacker H-100/K type products, it was suggested that Wacker send technicians to the Aycliffe Plant to demonstrate that the product could be produced there. Sinc the Aycliffe Plant autoclaves are 3,000 imperial gallon (3,600 United States gallons) glass-lined tanks with two Brumagim agitators on a central vertical shaft, the Bakelite personnel wished to be sure that the Wacker resin could be produced in this equipment.

The plant supervisor of suspension resins of Wacker and an associate came to the Aycliffe Plant, bringing with them the necessary raw materials to produce their resin. A series of eight runs was made. By the third run a very acceptable product had been made, but some further refinements were desired in particle size and a total of eight runs were required to arrive at the emulsifier system recipe used today.

In Table IV (page 27) are tabulated the H 100/K recipes as used at the Wacker Plant as modified for Aycliffe by the Wacker technologists, as currently used at Aycliffe, and as recommended by Wacker for trial in the South Charleston turbine-agitated autoclaves.

Note that the Brumagim type agitation results in a recipe using about 75 per cent of the concentrations of suspending agent and emulsifier that are used with the Pfaudler agitators in the Wacker Plant. Because of the higher shear expected with the South Charleston turbines, recommended concentrations of suspending agent and emulsifier are even lower. Also note that the only modification of the recipe at Aycliffe since its initial development has been to increase the catalyst concentration and, thereby, reduce the reaction time.

TABLE IV

WACKER-CHEMIE H 100/70 RECIPE
AS USED BY BAKELITE, LTD.

	As Used at Wacker	As Used at Aycliffe		Recommended for UCC Turbine Autoclaves
		Initially	At Present	
Monomer-Water Ratio	31:69	33:67	33:67	32:68
Polyvinyl Alcohol,* Per Cent of VCl	0.50	0.368	0.368	0.283
Mersolat, Per Cent of VCl	0.12	0.093	0.093	0.07
Dilauroyl Peroxide, Per Cent of VCl	0.08	0.078	0.11	0.08
Anhydrous Calcium Chloride, Per Cent of VCl	0.12	0.05	0.05	0.045
Calcium Carbonate, Per Cent of VCl	0.012	0.0088	0.0088	0.008
Temperature, °C	54	54	54	54
Reaction Time, Hours	19	19-3/4	16	19

*Wacker-Chemie Polyviol VZ-190

B. Process Changes at Aycliffe

For the first production of the Wacker resin at Aycliffe, the Wacker recipe was used while retaining many of the operating steps normally used at Aycliffe. The test autoclave was prepared by using extensive purging rather than by evacuation. At the end of the polymerizations, the product was recovered by conventional blowdown and wet stripping techniques.

Once it was established that a satisfactory product could be made at Aycliffe, licensing agreements were signed with Wacker and a team sent from Aycliffe to study the Wacker operation. As a result, several changes were made in the Aycliffe Plant to permit it to achieve the Wacker quality and higher efficiencies now regularly obtained. These changes were:

1. Revision and Relocation of Suspending Agent System

Because of the Wacker emphasis on suspending agent and emulsifier preparation, mixing and storage tanks for polyvinyl alcohol and Mersolat were relocated in the autoclave structure so that they could gravity feed a "charge wagon" similar to that used in the Wacker Plant. In addition, a DeLaval type BRH 3934H-22 centrifuge similar to that at Wacker was purchased to assure freedom from gels in the suspending agent and emulsifier solutions.

2. Simplification of Monomer Recovery System

The compressor for the monomer recovery system was piped up to strip vinyl chloride from the autoclaves through one of the wet stripping tanks which is now used as a foam tank. Vacuum type labrinth packing was installed on the compressor so that the autoclave could be stripped to about ten inches of vacuum. The rectifying column was removed and tankage for recovered monomer relocated near the water-cooled condensers. Great simplification of this system resulted.

3. Changes to Slurry System

The blowdown and wet-stripping tanks were vented to the atmosphere and steam heating of the wet-stripping tank eliminated. Wash connections were added to the Bird centrifuges.

In the present process the autoclaves are stripped at the end of polymerization. Then, because of the lack of gravity head, air pressure is used to transfer the charge to the blowdown tank. The slurry is then transferred by pump to the wet-stripping tank, which is now used as a wash tank. A low (36 inch) liquid level is maintained in this tank and some washing of the slurry is accomplished by dilution with water from spray nozzles at the top of the tank. No heat is used. Further washing is done through wash connections in the Bird centrifuges.

Attached to this report are copies of flow diagrams that outline revisions made to the plant at Aycliffe. Included are the changes made to the monomer recovery system and the new suspending agent preparation system that was installed.

C. Plant Performance

The data in Table V was prepared by one of the production supervisors at the Aycliffe Plant and represents current estimates of their performance and potential.

TABLE V

DVY 11 PRODUCTION DATA AT AYCLIFFE

Batch Cycle Times		
Reaction Time		16 Hours
Outcycle Time		
(1) Distillation	1.0	
(2) Blowdown	1.0	
(3) Remove Manheads, etc.	0.5	
(4) Rotor Jet Wash	0.5	
(5) Replace Bottom Manhead	0.25	
(6) Charge Water and Components	1.0	
(7) Replace Top Manhead	0.25	
(8) Pressure Test	0.5	
(9) Pull Vacuum	0.5	
(10) Charge VCl and Catalyst	0.5	6 Hours
Cleaning Time Apportion		2 Hours
		24 Hours

Cleaning Cycle

(1) Sellars Rotor Jet Wash after each batch.

(2) Quick manual clean by operators after five batches to make sure safety valve and bursting disc nozzles, etc., are clear. Also remove lump from agitator shaft and clear loose skins.

(3) Full scale manual clean every ten batches by day shift cleaners. Includes servicing of valves, instruments, etc.

Cleaning Times	5 Run Clean	3 Hours
	10 Run Clean	17 Hours
	Total	20 Hours

This is apportioned above at two hours per batch.

Charge Data	
Autoclave Capacity (3,000 Imperial Gallons)	3,600 U. S. Gallons
Charge Volume	90% Autoclave Capacity
Charge Basis	8,330 Pounds VCl
Monomer-Water Ratio	1:2
Catalyst Concentration	0.11% on Monomer
Temperature of Water	70°C Approximate

TABLE V (Continued)

Yield Data	
Yield Per Batch	7,270 Pounds Good Resin 230 Pounds Tails and Scrap 7,500 Pounds Gross Resin
Potential Number of Batches Per Week	35
Potential Yield of Good Resin	254,000 Pounds Per Week
Practical Yield of Good Resin (At 93 Per Cent Plant Utilization)	236,000 Pounds Per Week
Practical Yield of Good Resin Per Autoclave	47,200 Pounds Per Week
VCl Efficiency (Based on Good Resin)	90-92%
VCl Efficiency (Based on Gross Resin)	93-95%

This is 1.875 pounds per gallon per day capacity for good resin at 93 per cent plant utilization. In like manner, twelve 4,600 gallon autoclaves in the South Charleston Plant would yield a capacity of 38,000,000 pounds per year of good resin on a single product basis.

The change to the Wacker recipe has resulted in a decrease in the capacity of the flash dryers. In an Aycliffe flash dryer the former product, which was less porous, could be handled at rates of about 1,500 pounds per hour. The Wacker product, as produced initially with hot wet-stripping, was dried at 1,250 pounds per hour rates. With the current autoclave stripping procedure and cold Bird feed, drying rates average 1,050 pounds per hour.

D. Proposed Future Changes

One of the major inefficiencies of the current process is the use of autoclaves as stripping tanks. This adds a minimum of one hour to the cycle time, reducing the plant capacity accordingly. The Bakelite engineers considered using th blowdown tanks for stripping, but they were not of sufficient strength to contain the autoclave change nor stand a vacuum. At some future date, they feel they may install stripping vessels as a means of increasing plant capacity.

APPENDIX

Control Tests at Wacker-Chemie

In the Wacker laboratories, the following listed raw materials tests and resin evaluation methods were available for process control and resin quality determinations. Many of these tests were used non-routinely, in periodic check analyses, or in analyzing special problems. The tests which Wacker uses consistently and upon which they rely particularly for quality control information are noted "*" and will be described briefly. Supplementary and detailed information about these and other of their tests are included.

I. Raw Materials Tests

A. Fresh Vinyl Chloride

1. Free HCl (MOHR Method)
2. pH Value
*3. Polymerization Test
4. Aldehyde Content
5. Peroxide Content
6. Acetylene Content
7. Control of Insoluble Contamination (Dirt)
8. Iron Content

B. Recovered Vinyl Chloride

1. - Same as for Fresh Monomer
5.
6. Acidity, if pH is 3.0 or Less

C. Polymerization Water - Deaerated, Ion-Exchanged Water

1. Chloride Content (MOHR)

2. pH Value

*3. Drop Count Test

D. Polyvinyl Alcohol

1. Total Solids

2. pH Value

3. Saponification Number

4. Viscosity, Four Per Cent Aqueous Solution, 20°C

E. Nekal BX

1. Total Solids

F. Dichloroethylene

1. Neutrality

2. Density - To Determine Cis-Trans Isomer Proportions

3. Distillation Curve

G. Peroxide Catalysts

1. Lucidol Dibenzoyl Peroxide

a. Moisture Content

b. Peroxide Content

c. Iron Determination

d. Chloride Determination

2. Dilauroyl Peroxide

a. Peroxide Content

II. Process Control Tests

A. Polymerization Solution (Aqueous Medium)

1. Chloride Content (MOHR)

2. pH Value

3. Qualitative Test for Polyvinyl Alcohol

4. Aldehyde Content

5. Acidity

*6. Drop Count Test

III. Resin Evaluations

1. Chloride Content

2. K-Value Determination

3. Acetone Solubility

*4. Bulk Density, After Shaking

5. Apparent Density of a Fluxed Compound

6. Screen Analyses

*7. Heat Stability, Mill Test at 150°C

*8. Electrical Conductivity of Water Extract

9. Moisture Content

*10. Brabender Plastigraph Evaluation

11. Tensile Tests, Resistance to Tearing and Elongation

12. Preparation of a Press Plaque

13. Specific Indentation Resistance of a Press Plaque

14. Softening Point

15. Thermal Stability, by HCl Evolution

16. Water Take-Up

*17. Plasticizer Acceptance

18. Plasticizer Speed on Mill at 100°C

*19. DS-207 Stabilizer Tests

20. Color Test with Fuchsin Solution

I. Raw Materials Tests and Specifications

A. Vinyl Chloride Quality

The quality of vinyl chloride used at this plant appeared to be under excellent control. Most of the monomer is produc d from acetylene and HCl by the synthesis route at another part of the Burghausen Plant and the refined material pumped to the polymerization plant storage tanks. The balance of their monomer is purchased from outside sources, both in Germany and Italy.

The following criteria are used to judge the quality of their monomer:

1. Free HCl - Essentially free, test results nil.

2. pH - 5.5 to 6.5. This varies with the water used for scrubbing the vinyl chloride for the pH determination. A value 0.1 to 0.5 pH unit higher than the water control is usual.

*3. Polymerization Test - A period of 140 to 250 seconds is acceptable. This test consists of scrubbing a portion of uninhibited vinyl acetate with 50 grams of vinyl chloride vapor from a sample cylinder during a 45 minute period, followed by adding one per cent dilauroyl peroxide to an aliquot of the vinyl acetate. This catalyzed vinyl acetate is heated in a large test tube by an electric immersion coil until the attached thermometer reads a 50°C vapor temperature. Then the heater is removed and the time is measured by stopwatch from this moment until the vinyl acetate polymerizes violently. A control is run on unscrubbed vinyl acetate for comparison. In their apparatus, the vinyl acetate control runs 85 to 90 seconds. They grade the vinyl chloride quality by this scale:

140 - 250 Seconds = Very Good
250 - 350 Seconds = Average
350 - 500 Seconds = Moderate to Low
Over 500 Seconds = Poor

This test is run approximately once per day on monomer samples from both the fresh and recovered storage tanks. Both recovered and fresh monomer generally average around 180 to 190 seconds.

4. Aldehyde and Acetylene Content - Essentially nil. B th tests are made approximately once per week on fresh monomer in the storage tanks and spot checks are made on purchased material from the tank cars.

5. Peroxides - Essentially nil. This test is no longer required, since extensive experience has shown no peroxides are present.

6. Iron Content - Less than 0.2 ppm. Since the storage system is ordinary steel, periodic checks are made for iron by weathering about 5,000 grams in the dark (to prevent polymer formation). The residue is taken up and analyzed for iron. This test is used much more during periods of monomer plant upsets or when new equipment is being put into service.

B. Water Quality

The water for this plant is obtained from a canal which b gins at a nearby lake. The water is treated by conventional means of alum precipitation and sand filtration, followed by demineralization through double ion-exchange resin beds to remove both anionic and cationic contamination. It is deaerated and heated as described in the process and flow sheet section of this report. The following items are checked for water quality:

1. Chloride Ion - Less than 25 ppm. This normally runs from 5 to 10 ppm and is monitored daily. High chloride ion content is not serious in recipes to which calcium chloride is added, but for HH 100/70f the above limit is maintained.

2. Electrical Conductivity - Not over 0.3 micro Siemens. A micro Siemen is 10^{-6} $ohm^{-1}cm^{-1}$
(U.S. equivalent of 1 micro Siemen is 1 micromho)

3. pH - Range 5.5 to 6.5 from water treating plant.

4. Drop Count - 50-52 drops in their standard instrument. This simple empirical test measures essentially the surface tension and viscosity properties of water and the dilute aqueous solutions which comprise the polymerization media in suspension operations. The procedure amounts to counting the number of drops of the test solution which are emitted from a small pipette-like glass device with a capillary tip. Their particular device is calibrated for 50 ± 2 drops of water at 20°C. The water solution charged for the HH 100/70f recipe gives a value of around 60 drops before polymerization, and about 54 drops after polymerization. For H 100/65, typical values are 110 ± 5 before and 72 ± 5 after the run. This test is used primarily to monitor autoclave charging for errors. The charge control sample (item 4 of procedure) is taken primarily for this purpose. Each recipe has a characteristic "drop count" value which is known from experience. Deviations from these values in their operations serve to draw attention to possible sub-standard resin quality.

C. Quality of Other Raw Materials

1. Suspending Agents - The polyvinyl alcohol used by Wacker was produced in another part of the Burghausen Plant and batches of the material meeting their requirements were furnished as required. Specifications for this material were not obtained, but samples of the materials were brought back for comparison with domestic polyvinyl alcohols. The degrees of hydrolysis of their materials (91-92 per cent and 82-83 per cent) bracket the commonly available domestic grade (87-88 per cent) at the 20-25 centipoise viscosity level. See Table VI for a more complete comparison.

The Methocel 10 was standard technical grade material as supplied by Dow Chemical Company. No tests were noted for this suspending agent.

TABLE VI

COMPARISON OF COMMERCIAL TYPES OF POLYVINYL ALCOHOL

Source	Type	Viscosity,* Centipoises	Saponification Number	Degree of Hydrolysis	Remarks
Wacker-Chemie "Polyviol"	W 25 VZ 100	25	Approximately 100	91-92%	
	W 25 VZ 140	25	Approximately 140	87-88%	
	W 25 VZ 190	25	Approximately 190	82-83%	Used for H 100/K
duPont "Elvanol"	52-22	19-25	126-157	86-89%	Similar to VZ 140
	50-42	35-45	136-157	87-89%	Higher Viscosity Than VZ 140
Shawinigan "Gelvatol"	20-30	4-6	145-157	88-89%	
	20-60	21-25	126-157	86-89%	Similar to VZ 140
	20-90	35-45	126-157	86-89%	
Colton "Vinol"	PA-5	4-6	126-157	86-89%	
	PA-20	19-25	126-157	86-89%	Similar to VZ 140
	PA-40	35-45	126-157	86-89%	
Bordon "Lemol"	22-88	21-25	126-145	86-88%	Similar to VZ 140

*Viscosity in centipoises of four per cent aqueous solution at 25°C.

Not : None of the four United States producers have any commercial counterparts for Wacker's VZ 100 or VZ 190 materials. The 91-92 per cent or 82-83 per cent hydrolysis materials are not produced at all at any viscosity level and lower degrees of hydrolysis (73-77 per cent) are produced only at very low viscosities (1 to 4 cps).

2. Nekal BX - No tests other than the total solids were found for this material. This is a common industrial grade detergent in Germany and is purchased by Wacker.

3. Dichloroethylene - This chain transfer agent is used to obtain the lower polymer molecular weights which cannot be obtained by higher temperatures because of the 150 psig autoclave pressure limitation. No advantage of this material over the trichloroethylene used in our process could be seen from a concentration standpoint. Approximately 1.2 per cent was required to produce a $0.162\eta_{sp}$ resin at 59°C. In South Charleston production approximately 1.5 per cent of trichloroethylene is required to produce QYSJ, $0.145\eta_{sp}$ at 57°C.

   Dichloroethylene is not readily available in the United States and Wacker's use may be based on having the material at hand. They generally specify a distillation range and have a curve of density versus cis-trans isomer ratio, both of which they use to insure consistent composition in this raw material.

4. Peroxide Catalysts - The only catalyst in production use for suspension polymerizations is dilauroyl peroxide, which is purchased on the basis of accepted industrial standards. Apparently no tests are run by Wacker.

5. Mersolat Detergent - No reference to quality standards or tests on this material was noted. It is purchased by Wacker. A sample was brought back for comparison with domestic materials of similar nature.

D. Process Control Tests

The only control tests in evidence for the polymerization w re run on the charge control sample described previously under "Drop Count". Certain recipes also required low chloride in content and particularly pH ranges for which the same sample was used. The expected range of pH values for each recipe is shown in Table I.

The other tests listed are nonroutine and may be run only if unexpected results are obtained in a particular batch of resin. The charge control sample is retained until a quality disposition has been made of the resin, should it be necessary to try to trace causes for unusual behavior.

E. Resin Tests and Evaluations

Of the tests listed, the majority are similar in principle and well known to our resin evaluation people. However, several methods require some explanation.

1. Bulk Density - All of Wacker's bulk density figures are determined on a sample compacted in the measuring graduate by a concise vibrating technique. Their values could be expected to be about 10 per cent higher than the apparent density values on the same resin in our laboratory.

2. Heat Stability, Mill Test at 150°C - This is the only routine evaluation of the initial color and ultimate stability used by Wacker. The test consists of milling an unstabilized compound at 150°C on a two roll mill and taking small swatches of 20-25 mil sheet at times of 1, 2, 3, 4, 5, 10, and 15 minutes on the mill. These samples were then evaluated visually to determine the general level of initial color and holding power.

   Further, by the addition of a pinch of carbon black and 10 minutes more on the mill, with careful mill operation, the operators were able to sheet off a smooth, bubbl - free, dark gray film which was visually appraised for fisheyes and hard resin particles.

3. Electrical Conductivity of Water Extract - In the absence of a suitably inexpensive and reliable method for testing the electrical properties of resins or compounds directly, the Wacker people have relied on measuring the electrical conductivity of a water wash from the dried resin. A recent simplification of this method involves slurrying a small amount of resin in 20 times as much conductivity water, agitating for one hour at room temperature, and determining the conductivity of the slurry directly. A blank determination on the water used for the slurry is always required.

Wacker's upper limit of conductivity for electrical grade resins by this test is 30 micro Siemens (30×10^{-6} ohm^{-1} cm^{-1}). The conductivity water used should not exceed 0.1 to 0.3 micro Siemens conductivity.

The Wacker laboratories were working on a direct measuring technique for electrical properties of resins and/or compounds, but their developments were not ready for discussion.

4. Brabender Plastigraph - These machines were used extensively in their laboratories. Most of them were German-made models. They were used routinely for two purposes:

   a. To assess the ease of processing of a resin.

   b. To determine the normal melt plasticity-time-temperature curve of a particular resin compound.

   The first test took a lightly plasticized pigmented mixture and subjected it to hot processing at 125°C for 10 minutes after which the fluxed resin was removed, cross-sectioned with a sharp knife, and examined with a magnifying glass for hard white particles and grainy appearance. This was primarily a qualitative screening test to monitor the general level of processing speed and ease of resin compounding.

   The second test was run to evaluate blends for special customer requirements, particularly with the higher K-value resins.

5. Plasticizer Acceptance - This was a roughly quantitative test of the absorption of plasticizer in the resin at room temperature. A five gram sample of resin was hand mixed in a porcelain evaporating dish with a spatula, adding increasing amounts of DOP plasticizer from a burette until a small amount of the mixture, when pressed between the fold of a piece of filter paper, left a detectable grease spot. The ratio of milliliters of DOP to grams of resin was reported at this end point.

The Wacker people had a comparison of this test with several published absorption tests using excess plasticizer and centrifuging. Their comparison indicated that the above procedure very closely agreed with the more elaborate tests in terms of arranging a group of resins in relative order of increasing plasticizer acceptance.

6. DS-207 Stabilizer Tests - This test was a qualitative examination of considerable value to indicate the type of suspending agent used in the preparation of competitive resins. The test was based on certain suspending agents showing different shades of color in milled compounds containing a small amount of DS-207 lead stabilizer. A compound of resin and DOP plasticizer containing about one per cent DS-207 was milled at 175°C for five minutes and a small sheet was sampled. From the characteristic color shade, an estimate could be made of the suspending agent used:

   a. Clear, no discoloration - gelatin or Cellosize.

   b. Yellow cast with various degrees of haze - polyvinyl alcohol.

   c. Dirty gray or brownish cast, somewhat clear - methyl cellulose.

   Obviously, some experience with resins of known suspending agents would be required for more competent judging, but the test was considered short, simple, and relatively reliable.

POLYVINYL CHLORIDE SUSPENSION RESINS

THE WACKER CHEMIE PROCESS

REPORT OF PLANT VISIT, NOVEMBER, 1959

FIGURE 1

Relationship of Fikentscher K-Value to Specific Viscosity
Polyvinyl Chloride Resins at One Concentration
c = 0.200 gm/100 ml Nitrobenzene