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CONOCO

Interoffice Communication

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Subject A HISTORY OF THE TECHNOLOGY OF PVC RESIN WITHIN CONOCO

This recitation will be as best I can remember the events and their timing. Many of these events are contained in reports written while the PVC affairs were under the designation of Thompson Apex or later under Conoco Plastics. A review of the reports on PVC resin from these sources would be potentially useful but could be extremely time consuming for the value that much of it will now present. I will attempt to recapitulate the basic history.

There are many events connected with the history of the resin technology which occurred as specific plant problems. Their solution may have evolved from pilot plant development work, plant experimentation, or from some intuition, which suggested plant changes that were subsequently made and which were effective. I doubt very much that any records of this kind of thing exist in the plant. Records will exist in part, however, in formal reports and in IOC's on the specific subject at the time. Since many of these events were of a very short term and some existed over quite a long term, it may be difficult to piece them together from written work. I will endeavor to comment on some of these as we go along.

I. Thompson Apex

Conoco got into the resin business in 1964 by the acquisition in September of the above-named independent company. Thompson Apex was, at that time, a company with plants in Assonet, Mass., and Aberdeen, Miss. The total capacity was about 250 million pounds. There were three reactor buildings in Assonet each of which contained twenty 2,200-gallon reactors, glass lined. Aberdeen contained two of these buildings. The technology in 1964 might be considered basic and possibly representative of the industry. Larger reactors were in use elsewhere, but the size we had at that time was not uncommon. In fact, B. F. Goodrich and perhaps others operated some thousand gallon reactor plants. The larger sizes then in use in the industry were 3,750, 5,000, 6,000, and 7,500 gallon.

The technology by today's standards was elementary. Reactors were charged while open, first with the water and secondly with the initiator which was in all cases lauroyl peroxide. The suspending agent was charged with the water in an unbelievably crude manner. The accuracy had to be in doubt, but little account was taken of this. The suspending agent in common use for all resins was what we would now call Methocel F50.

The resin types made at that time were the following:

A. The 5000 series were general purpose suspension homopolymers. They ranged from specific viscosity 0.20 to 0.52. The lower molecular weight resins were made using trichloroethylene as a chain transfer agent. The intermediate resins had specific viscosities of 0.26, 0.30, 0.35, 0.38, 0.41, 0.44, and 0.46. Certain resins were made to have a particularly coarse particle size. These had a five as the terminal digit. The primary such resins were 5385 and 5445. Another resin which was not only relatively coarse in particle size but had an unusually high dry time was 5446. A normal particle size with an exceptionally high dry time was 5411. Actually, these numbers were not employed at that time. This numbering system was derived later when Conoco Plastics became the effective operating company.

In the Thompson Apex time, the standard resin was relatively fine with perhaps 30 percent or more through the 140 mesh. These were considered applicable for most flexible uses, particularly calendering. The coarser resins came into being at the request of what was perhaps the more sophisticated user companies, and the resins were often designated by number for that company (e.g., 500AR was Anaconda Resin). Essentially all of our resins now are coarse resins by those standards and thus have five as the terminal digit. "Coarse" meant 10 percent maximum through 140. That maximum has faded over the years to a larger number.

The variability from batch to batch in particle size was quite great in the 2200 gallon technology but was dialed out to some degree by batch blending of seven individual batches. However, because the probabilities eventually covered all combinations of individual batch particle size distributions, the variability from lot to lot within each blend tank was substantial. This was a source of some concern but was basically beyond control because of the inherent variability of the process and an unwillingness to improve it to any degree.

A typical 5385 in the Thompson Apex time (it would have been called Trulon 510) required around a 12-hour polymerization time. This included a 30- to 45-minute heatup. The monomer was charged after the reactor had been closed and evacuated. Incidentally, the practices at the time resulted in very high

monomer concentrations in the work area. The exact value of these remains unknown because no measurements were made, but excursions to 1,000 ppm must have been common.

B. Vinyl acetate copolymers were also produced under the 7000 designation. These ranged from nominal 3 percent to 15 percent acetate content. That is, resins were generally of two types, 3 to 5 percent and 13 to 15 percent. The low acetate copolymers were made by charging all of the monomers at the same time. The high level acetate resins were made by charging some of the vinyl chloride initially but adding the remainder in three shots. (Incidentally, the exact charge size and shot size for all of the resins I will be talking about can be found in the formula books which are on record in Dave Porchey's or Pete Schwab's office. It is also possible to view the evolution of the formulas in the small reactors by reviewing these files. I am not sure that it would be worthwhile.)

Acetate copolymers were made not only in varying acetate contents, as noted, but also according to molecular weight (specific viscosity). Most copolymerizations produce a lower molecular weight at a slower rate than either monomer would polymerize to give its homopolymer. (This is simply in the nature of the kinetics of copolymerization where cross propagation tends to lead to reduced rates and increased termination.) I will not go into the applications of the copolymers according to acetate content and molecular weight specifically except to say that the higher acetate content generally went into flooring and the lower acetate into calendering of rigid film for credit cards. There was some calendering of copolymer sheet also. The acetate copolymers posed a major heat stability and color problem. The higher the acetate, the worse both.

It can be well imagined that stripping of monomer from a copolymer, particularly the high acetate types which were of glassy nature, was extremely difficult, and much acetate remained behind, perhaps as much as 1 or 2 percent. This caused a sticking problem and a problem with high volatiles. Color was solved, if you can call it that, by adding an epoxidized soy bean oil. This, however, created certain tackiness problems which were not easily resolved. The tech service input to acetate resins was quite high relative to homopolymer.

Thompson Apex and subsequently Conoco Plastics made the mistake of attempting to make copolymer in the same reactors and through

the same downstream isolation mechanisms as the homopolymers. This invariably led to the contamination of copolymer by homopolymer and a myriad of resulting customer complaints. Conoco Plastics was a worse offender than Thompson Apex, who knew better but occasionally succumbed. Conoco Plastics knew better also, chose to ignore the knowledge, and always succumbed.

Copolymer posed two other serious problems in manufacture. One was a much greater tendancy to build up on the reactor walls. The other was a continuation of that kind of thing by a greater tendancy to set up completely into one large mass in the reactor. Copolymers exist, of course, to provide easier processing and are by nature lower fusing which made them more susceptable within the reactor.

C. Plastisol resins were made by a process just recently developed when Conoco moved into the operation in a direct sense in 1967. The process was not a good one. It involved in-situ formation of a seed polymer in the presence of sodium tridecyl sulfate as the emulsifier and potassium persulfate as the initiator. Vinyl chloride was added essentially on pressure under starved conditions. This in itself is no catastrophe, but the spray dryer that was used was.

The latter was a product of Anydro of Denmark and fabricated in the U.S. by another company owned by the original owners of Thompson Apex. It was probably more responsible for the poor quality of the plastisol resins generally than any other thing. Plastisol resin technology is extremely complex, and the resins bear no resemblance to suspension resins. It is difficult to even make a plastisol resin which bears a resemblance to a competitive plastisol resin. Thompson Apex with its close connections to the PVC consuming industry was able to establish a moderately good business in plastisol. Basically, only two molecular weights were made. Specific viscosities were 0.46 and 0.35. Although competitors offered some acetate copolymer plastisol resins, we did not, for which I am thankful.

D. Extender or blending resins were also developed under the 8000 designation. Essentially, only one was produced. These are very fine, nonabsorbant resins. The particle size is preferably on or through 200 and little or nothing above 140. The objective is to blend these with plastisol resins and reduce the viscosity of the latter in plasticizer. They were sold only at a small

premium over suspension resins and reduced the raw material cost to the plastisol user. Two processes were used for these. One involved a simple suspension process using a mixture of two kinds of gelatin as suspending agent. The other involved blending the monomer and water with lauroyl peroxide and Methocel suspending agent in one reactor and passing it through a Manton-Gaullin pump which would homogenize the mixture and produce a very fine VCM droplet. This was a very difficult operation and was never operated sucessfully before we parted company with Thompson Apex. The extender resin business had really not gotten off the ground before the latter occurred.

E. Another kind of resin, the 6000 series, was a very highly absorbing homopolymer paralleling the 5000 series in molecular weights. It was very fine in particle size and low in bulk density, e.g., in the low 20's. The purpose of this resin was to absorb high levels of plasticizer without the application of heat to give a dry powder. This occurred fairly slowly relative to the heated process used with general purpose 5000 resins but permitted those still in the business with cold plasticizer blending facilities to operate those facilities. The suspending agent was Methocel F50 combined with T-177, a strange surfactant produced by GAF. The 6000s were not destined for a long-term future.

II. Conoco Plastics

In 1968, the separation of Thompson Apex into two parts occurred with the sale of one part to Olin Chemical and the Fain group and the retention by Conoco Plastics, newly created, of the Southern facilities. Conoco Chemicals set out to create essentially the same product line.

Conoco Plastics undertook to do two things immediately. One was to build another small reactor building to increase its capacity. This gave the Aberdeen plant three small reactor buildings. It installed plastisol resin equipment adjacent to one of these buildings via the addition of the spray dryer and grinding equipment, duplicating fully the facilities in the north. This was a tragic error and came in the face of solid knowledge to the contrary.

Before installing the plastisol facilities, Conoco Plastics undertook an extensive development in spray dryer evaluation. Plastisol latex directly from the reactors was obtained from Olin and evaluated at the spray dryer manufacturers test laboratories. A Swenson dryer was the probable best choice although any of the three types tested

(the others were Bowen and Niro) were clearly better than the Anhydro. Nevertheless, because the Anhydro could be had more rapidly and more cheaply and would be well understood mechanically, it was selected to the utter detriment and probable demise of the project.

Vinyl acetate copolymers and 6000 series resins were also manufactured at Aberdeen. The 8000 resin was begun but was never really undertaken. The Manton-Gaullin pump route was selected, and such a pump was installed but never piped up. The plant was highly reluctant to get involved just as they were when the plastisol plant started up. The latter was the most blatent display of manufacturing intransigeance I've ever seen.

In due course, both acetates and plastisol and, of course, extenders were all abandoned as being unprofitable in the light of the productivity that could be achieved with the general purpose homopolymer.

To return to homopolymer, immediately in 1968 Conoco Plastics set out to increase its productivity by employing the latest initiator technology. This involved the so-called fast initiators which were peroxydicarbonates. These were so active as to require refrigeration to prevent explosion and fire. Thompson Apex had refused to allow such initiators on the premises. We knew they could be used safely and proceeded to do this. The changeover was accomplished essentially by Pete Schwab and myself in the matter of a month. (Lauroyl peroxide was used for the low molecular weight polymers until later on when L-11 was used.) The use of the fast initiators across the board where applicable, which accounted for 85 percent of plant production, raised the productivity of the plant greatly by dropping 12 hour polymerization times to eight hours and with chilled water to six hours. The product quality improved at the same time in that the particle size became coarser, and less suspending agent needed to be used. There was a temporary setback in bulk density, but that was quickly corrected by the particle size change and plant experience.

This change in initiator was accomplished without elaborate deployment of forces because we knew what we were doing and because the plant was won to cooperation in the changeover and ran the necessary experiments as rapidly as possible. In most cases, we did not inform our customers because the resin was improved in every way, and it was not deemed necessary to make a public disclosure. For one thing, the heat stability improved because there was markedly less residual initiator in the product.

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III. Conoco Plastics and The Technology Breakthrough

In 1969, Conoco Chemicals began a build-back of PVC capacity to try to gain the stature it had when it had plants in both the North and the South. A third 20 reactor building was constructed at Aberdeen as already noted. At this time, an emphasis was put on producing low-gel resin because the condition of the new reactors was, of course, extremely good, and it seemed reasonable to concentrate that building on low-gel resin production. This was part of an effort to gain some higher quality resin business with some possible modest premium over pipe grade.

The technology for producing low gels was well understood at that time in the sense that it was recognized that scrupulously clean reactors prior to charging was the key. There were other negative factors which were also known: e.g., letting the conversion run to more than 85 percent (a pressure drop to less than about 85 psi for a 5385). To counter this, part of the low-gel program involved running to about 90 psi pressure. Another example was maintaining an isothermal polymerization temperature. It was shown conclusively that when runaway batches were compared to isothermal batches, the latter invariably had much lower gels. It was felt that the nonisothermal batches incurred both too high a conversion and a tendency to lower porosity simply because of the softening effect of the higher temperature. Filtration of monomer was also recognized to be vital to avoid polymer particles from the recovery system or from fresh monomer where some polymerization might have occurred.

The plant was in a sad state of manufacturing competence at the time, unfortunately, and the exertions required in such a program were not destined to succeed. Besides that, all the requests for caution in cleaning and dealing with the new reactors were for naught, and they very quickly became as abused and the glass as scarred as the old reactors.

In early 1969, a team visited Pechiney-St. Gobain as it was called at that time. This company had exploited the mass process for PVC. We came to know the mass process in intimate detail and concluded that there were several negatives to taking a license. One is that the product could not really be made economically in molecular weights above that of pipe resin. The license fee made the cost of resin excessive. Besides that, the idea had germinated that we could just possibly undertake our own development of a large reactor suspension process. These ideas were debated between Bob Allen,

Pete Schwab, George Tillson, Gordon Ferguson, and myself. In 1970, in the spring, we installed a large reactor identified as the D300 vessel, equipped with a bottom entering agitator, overhead condenser, and four symmetrically-placed, vertical 12-inch baffles. The baffling and agitation had been decided upon after numerous conversations with agitation suppliers, such as Pfaudler and Mixco (Lightnin). The latter company was highly knowledgeable in a theoretical sense, it appeared, and the agitation originally installed in the D300 was their best recommendation for PVC.

At the same time, various other Methocel suspending agents had been tested, K35 and E15 in particular. E15 gave an extremely porous resin, with excellent dry time for a given conversion, generally lower gels than F50, but with the negative that more had to be used and foaming was a problem in recovery. K35, on the other hand, was very efficient. Foaming was of some difficulty, but no worse than F50, and perhaps better. The bulk density of the resin increased, and the particle size tended to be somewhat more grouped. The porosity of K35 resins, however, was significantly less.

The prospect for making a higher bulk density resin also became apparent. In dealing with Certain-Teed, we encountered the competitive Goodrich product, which had a bulk density (apparent) of around 35 to 36 and a compact bulk density of around 40. We had some history of making high-bulk density resins in the pilot plant at Thompson Apex, so applied that in Aberdeen. Using polyvinyl alcohol, it was possible to get bulk densities such as those quoted above in the 2,200 gallon reactors at Aberdeen. Certain-Teed was eager to try this, and we sold them in the vicinity of 2 or 3 billion pounds, which they evaluated almost completely in their Waco, Texas, plant. The conclusion after several months was that the scrap rate, because of impact failure, was unusually high, and they rejected further use of the resin. In the meantime, we had continued to experiment in the pilot plant at Wilton and examined the Goodrich product in greater detail. It was obvious that our resin lacked porosity, had a translucent and/or glassy character in part, and that this was causing fusion problems. The Goodrich resin, on the other hand, was porous, opaque, and had a lower dry time. We found that a mixture of polyvinyl alcohol and F50 or E15 in the pilot reactor at Wilton would give a bulk density that was virtually linear with the ratio of suspending agent. The more polyvinyl alcohol, the higher the density and the lower the porosity. A ratio of about 65/35 to 75/25 of PVA to F50 gave resin that was in the 35 apparent density range. We produced

this in small reactors in Aberdeen in mid-1971 and found that it was extremely satisfactory at Certain-Teed (eventually, the business fell apart, but primarily because of business reasons which will not be discussed here).

Incidentally, the finishing touches on that high-bulk density resin development occurred in the Vinatex plant. They also had a need for high-bulk density resin. We brought them our pilot results, and they were eager to conduct the plant tests to see if it worked. We found that it did. They executed a few local refinements and have ever since had a great deal of success in the pipe industry in the UK.

Experimentation began in the Spring of 1970 in the D300. The tenor of the experiment was conservative. We would, for example, run at water-to-monomer ratios of 6 or 7 to 1. The initial results were very promising in that a good looking resin with good particle size was very quickly established. As we then dropped the water-to-monomer ratio, we noticed that the average particle size began to increase, such that more suspending agent had to be added. Several times extremely coarse resins on the edge of catastrophy resulted. We found that by the time we had gotten to a water-to-monomer ratio of 2 to 1 or slightly less, the amount of Methocel was in gross excess to what we normally encountered and the resin would not extrude satisfactorily. We tested it in large quantities at Carlon and were able to reproduce the poor extrudability. This phenomenon, the need for increased suspending agent at lower w/v ratios, became known as the D300 effect. (The suspending agent was F50, incidentally.)

We experimented extensively with changes in the diameter and shape of the agitator blades and with the speed of the agitator. We could not get through the D300 effect. I then came across an article from Japan on the polymerization of styrene in suspension, which contained the seed of an idea that the baffling was perhaps the most important part of the system. Acting on this, we began to take out the baffles and thin them down. We took out two of the four installed 12-inch baffles. This made no marked effect. We cut the remaining two to a 6-inch width and the effect was dramatic. The D300 effect disappeared.

We were able to proceed from a 7 to 1 water-to-monomer ratio to a 1.3-to-1 ratio without increasing the concentration of suspending agent relative to monomer. This was the key breakthrough. After a few more refining experiments, we ended with two 3-inch

baffles. It was interesting in the course of this sequence to note the physical change in the vortex of water agitated under the varying conditions we evaluated. In the case of the four 12-inch baffles, there was no vortex. The surface was simply a swirling, disorganized mass. As the baffling decreased, a vortex began to appear until at the end a very deep vortex, with what could be described as a high degree of swirl or laminar flow, resulted.

The theory we felt may explain what happened is that in the completely disorganized turbulent mass created by the original baffles, collision of monomer droplets was more frequent for a given population density. As we decreased the water-to-monomer ratio, the population density of the droplets increased greatly and the suspending agent was no longer effective in keeping them from sticking when the collision frequency brought them together. Hence, large concentrations of suspending agent were necessary.

In the vortex laminar system, the particles traveled in essentially the same direction with much less mutual encounter, hence less tendency to stick together and less suspending agent needed to prevent that from happening. If the theory, which is intuitively attractive, is not correct, the facts as noted are.

Construction began on the Oklahoma City plant in late 1970, well before the D300 problem had been solved. There was, therefore, some pressure to solve the problem. The Oklahoma City plant started up in May of 1971, with essentially no problems. The AFE capacity for a four reactor plant had been stated at 67.5 MM pounds. We knew that with operation of the condenser and a water-to-monomer ratio of about 1.4, we would have a capacity of 110 MM to 120 MM pounds. We also speculated that with refinements and cautious forward movement in water-to-monomer ratio and reaction speed we could expect 150 MM to 160 MM pounds. This is not far from the capacity of four reactors today operated with due regard to quality.

The leap from 2,200 gallon to 16,500 gallon reactors was a remarkable event. The industry had regarded heat removal as an impenetrable barrier to increased reactor size, i.e., greater than 7,500 gallons. Use of a condenser was universally held to be impractical. These wisdoms were entrenched, and besides, there was the agitation scale-up problem which was regarded as potentially as limiting as the others. It was with a sense of triumph that we made our first full size batch (1.3 w/v) at a standard [F50] and fully in spec on product in a poly time of about twelve hours. Shortly after that,

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we learned of Shin-Etsu's system with 35,000 gallon reactors, which was a little deflating. But we now know that our productivity on lbs/reactor gallon/yr basis is greater than Shin-Etsu's and probably greater than any other in the industry.

The use of a condenser did not originate with the D300. We erected a condenser on one of the 2,200 gallon reactors via a dome nozzle, requiring that the condenser have an angled offset to clear the agitator motor. Plugging was a severe problem and the condenser was removed. Vinatex tried its hand in a similar way, going so far as to install about twenty condensers. They failed, too.

The D300 condenser success is not 100 percent. Tube plugging does occur but only a few at a time. Occasionally, the plugged tubes must be reamed or brushed out, but the trade-off of downtime to productivity gain is very favorable. We think success may be due to the fact that there is a straight flow of condensed VCM with a center-mounted condenser, giving a self-washing effect not created in the angled condenser.

With a highly effective condenser, the temptation to use high [initiator] is great in order to increase the poly rate. Poly times of 2-4 hours (isothermal) are a possibility. Experience taught us, however, that heat stability suffered because of high residual [initiator] in the final resin. This dogma may now have been overcome by use of killing agents, antioxidants, and steam stripping which conspire to destroy most of the residual initiator under conditions where the resin is protected. If true in fact, apart from the reason why, it will be a productivity breakthrough.

As soon as the initial experiments were completed in the D300 in 1970, it was turned over to Production because the capacity was needed. The reactor ran very successfully. We continued to monitor the production runs and suggested and supervised cautious experimentation. We found, for example, that 100 percent recovered monomer could be charged and successfully used. The same events occurred with recovered monomer as did in the small reactors; that is, the particle size became finer and the suspending agent concentration had to be decreased as the percentage of recovered monomer increased. This observation had, we knew, been made by others in the industry.

After the initial successes with the above-mentioned high-bulk density resin, a campaign was launched in the D300 to make that kind of resin. Despite numerous efforts at suspending agent and

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agitation changes, we found that we could not achieve any success. The resin came out with a totally abnormal particle shape and structure, resulting most frequently in what we came to term grape cluster, which would be large agglomerates of smaller particles. The bulk densities, because of the unfavorable shape factors of the particles, were in fact lower than normal rather than higher. We speculate today that the hot charging method used in the D300 was possibly the problem. For example, unlike the small reactors, the initiator was not bombed in at room temperature followed by heat up; rather, the batch was hot as charged and the initiator was bombed in under those conditions. This means that distribution of the initiator between all of the monomer droplets is difficult to accomplish on a uniform basis. We think that this may have distorted the type of particle size when the polyvinyl alcohol suspending agent was part of the system. We think that polyvinyl alcohol-coated droplets are more difficult for initiator droplets to penetrate.

Incidentally, another basis for not getting good gel results is poor distribution of the initiator such that a few of the monomer droplets contain a large part of the initiator molecules, which will lead to a rampant overpolymerization in those overcharged droplets. This assumes that redistribution of the monomer by collision of droplets occurs significantly slower than the initiation of polymerization. It is a fact, certainly, that high concentrations of initiator in the pilot plant lead to salt-and-pepper effect in the final resin. We attribute that to individual droplets that become raging infernos of polymerization, resulting in individual overheating and poor heat stability, with resultant darkening.

Several other significant steps were taken in the large reactor. The 5305 resin was made in what was felt to be commercially acceptable rates and reactor charge size. Likewise, 5446 was made successfully. By defining those outer limits on viscosity by definition, any intermediate viscosity resin was defined as makeable. I have no doubt that much higher and much lower viscosity general purpose suspension resins could be made also, and that to do so would not be a major task.

In 1973, Tenneco, a company you may be familiar with, undertook licensing discussions with us. There were two problems with resin produced in the Oklahoma City plant. The volume resistivity was not sufficient and the gel content of the resin was extremely high. We set out to solve the VR problem at Aberdeen and produced

satisfactory resin (resistivity of greater than 2×10^{14} ohm-cm). This was accomplished by filling the reactor at least twice with deionized water, swirling and dumping. The charge was finally made with deionized water also. The resin not only had the good resistivity values but was exceptionally low in gels. Thus was born the difficult way to make low-gel resin in the large reactors, namely, by swirling to remove trapped resin particles from the prior batch.

Also interesting! JTF

The method described was not, unfortunately, satisfactory for either volume resistivity or gel reduction, and Tenneco opted for a Japanese process. (Shin-Etsu)

At this point, as you know, the volume resistivity question is now being pursued using nondeionized water that is within a hairs-breadth of success. Gel levels are at a reasonable level for all flexible purposes except high-grade packaging film. They could probably be rendered satisfactory for that if a campaign was launched using a clean wall formula and a more thorough rinse system. It is possible still that a swirl is necessary, but I think that may be avoided.

Sounds familiar!

One historic point should be noted. While we were at Thompson Apex and subsequently at Wilton (Conoco Plastics), we carried forward a program to make what we termed a solution copolymer. This means an acetate copolymer (about 13 percent) which could be dissolved in toluene-MEK to give a sparkling clear solution not in need of filtration, which could be used in such applications as coating the inside of beverage cans. Carbide is about the only participant in this business. When general purpose PVC sold for 10 cents, the solution grade copolymers were selling in the 40's or 50's. We used a suspending agent of the Ganex variety from GAF. This was a vinyl acetate-vinyl pyrrolidone copolymer. This material was soluble in the aforementioned solvents, which Methocels are not. Therefore, the copolymer was clear in that solvent mixture. Carbide's product, incidentally, was made in a hydrocarbon solvent such as butane and did not use a suspending agent; therefore, did not have the same problem. However, a suspension process would obviously be preferred for its economics. Unfortunately, we were never able to get a truly good solution copolymer in a plant reactor. The reason was not clear but the problem was. There was always an apparent conventional homopolymer contamination. Thus, it would appear that this appealing product line would have to have a much more sanitized plant environment than is possible in a plant where homopolymer and copolymer are made in the same systems.

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Much effort has gone into the large reactor system in the last several years. Many improvements have been made and are very useful, but no really new and unexpected events have occurred except for the prospect that heat stability can be decoupled from high initiator concentration. It would be worth noting, however, the development in catalyst technology beyond the simple use of a single peroxydicarbonate. The understanding of the basic kinetics has vastly increased. Much experimentation went on with dual initiators to try to take advantage of the slower rates that normally prevail at the beginning of a polymerization (the detail of the kinetics of vinyl chloride polymerization should be considered separately rather than here). It is certainly possible to use the cooling capacity more effectively by arranging the heat release to occur at a relatively uniform rate rather than in the increasing manner of single initiator. This can be done with certain initiator mixtures, such as ACSP* combined with a peroxydicarbonate. However, ACSP is so active that charging it into a hot reactor system with the batch already at temperature in effect leads to such rapid destruction of the ACSP that no or very little benefit can be had from it. It is thought that the ACSP simply does not get thoroughly mixed before it decomposes in a wild flood of ineffective radicals. One way around this is to mix the initiators with the VCM before the latter is charged. Pilot experiments where such mixing occurs just as the VCM enters the reactor have given favorable results with ACSP/peroxydicarbonate mixtures, but this approach presents a formidable engineering problem and has not been considered in some time.

No other initiator combinations have been found which are really commercially promising. However, some of the more recent materials such as the t-butyl perneodecanoate initiators do give a flatter heat evolution by themselves.

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*ASCP = acetyl cyclohexanesulfonyl peroxide, $C_6H_{11}SO_3OCOCH_3$.