Reprinted From The Journal of The American Medical Association
August 21, 1967, Vol. 201, pp. 577-581

Occupational Acroosteolysis

Report of 31 Cases

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In 31 cases of acroosteolysis of the hands of workmen associated with vinyl chloride (CH_2CHCl) polymerization processes, the osteolysis was specific to the distal phalanges of hands and was frequently associated with Raynaud's symptoms. Affected personnel ranged in age from 26 to 47. The disorder is believed to have resulted from a combination of physical insult, chemical insult, and personal idiosyncrasy. The specific causes are unknown. The prevalence was found to be less than 3% among employees performing similar work. No cases were found in workmen using or processing the polymer or manufacturing commercial resins.

During mid-1964, several complaints came to our attention of soreness and tenderness of the fingertips of workmen in a manufacturing plant polymerizing vinyl chloride (CH_2CHCl). Comprehensive examinations of these individuals revealed nothing of significance except a "Raynaud-like phenomenon" of the hands, and in some cases, definite changes of the distal phalanges were apparent on roentgenograms of the hands. Since then we have observed additional cases of this unusual syndrome. It is the purpose of this manuscript to summarize our observations.

Description of Syndrome

To date we have observed 31 cases of hand disorders among 3,000 personnel involved in vinyl chloride manufacturing and polymerization. All have been men, between the ages of 26 and 47. We have not observed any ethnic or racial tendency for the syndrome. The great majority have been characterized by two common factors: symptoms likened to those ascribed to Raynaud's phenomenon and acroosteolysis of the distal phalanges. A few have had no symptoms but have the roentgenographic evidence of acroosteolysis. Several of the patients have external skin lesions on the dorsal surfaces of the hands and forearms, with a rope-like appearance resembling changes sometimes seen in scleroderma. Some have clubbing of the fingers. Only a few of the cases have sought medical attention because of symptomatic complaints; the majority have been found through x-ray examinations of the hands.

A summary of the physical findings of the observed cases is shown in Table 1, and a detailed description of the two predominantly common symptoms follows:

Raynaud's Phenomenon.—This symptom complex has occurred in varying degrees, with one or both hands involved. Generally, its effect is observed as marked discomfort on exposure to cold. None of the cases have exhibited vascular changes of the feet. A unilateral sympathectomy performed on one of the most seriously affected cases relieved most of the symptoms on that side. The acroosteolysis was not altered by the sympathectomy.

Roentgenological Changes.—The most unique characteristic of this syndrome is the unusual roentgenological findings. These are described as acroosteolysis and are illustrated in Fig 1. It may be present in all of the fingers and readily observable, or only in one finger and barely discernible, as illustrated in Fig 2. X-ray films of the feet, as well as those of the long bones and of the skull have been made in some of these cases, with no osteolysis found other than in the distal phalanges of the hands.

Acroosteolysis is a rare clinical entity, with only 72 cases of the familial type reported up to 1965, according to Cheney in his excellent review.[1] The diagnosis of acroosteolysis requires expert roentgenological technique and knowledge. It has been our observations that early cases of acroosteolysis will be missed by the roentgenologist not familiar with this condition. All of the cases on which we are reporting have been confirmed by at least two experienced roentgenologists working independently.

We established the following roentgenographic criteria for our diagnoses. These are the result of our having viewed several thousand x-ray films of the hand in our search for the cause of the syndrome.

1. General: Roentgenographically, acroosteolysis, as found in workers who are exposed to vinyl

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chloride and polyvinyl chloride manufacturing processes, is somewhat different from that found in familial osteoporosis with acroosteolysis and in familial osteosclerosis with acroosteolysis. In osteoporosis with acroosteolysis there may be compression fractures in the spine, and basilar impression of the skull, along with destruction of the midphalanges. None of these findings have been seen in these workers. The changes in the distal phalanges are similar in both conditions.

Osteosclerosis acroosteolysis observed by Andren et al[2] (University Hospital, Malmo, Sweden) in twins showed diffuse sclerosis, with cortical thickening of the shafts of the long bones and clubbing of the metaphyseal ends. The phalanges of the hands and metacarpals were foreshortened, and the distal phalanges showed acroosteolytic changes. The feet showed the same changes, except that the distal phalanges were not fragmented.

There has been no evident destruction in the mid or proximal phalanges of the thumbs or fingers of these individuals and no evidence of a lytic, destructive lesion in the feet.

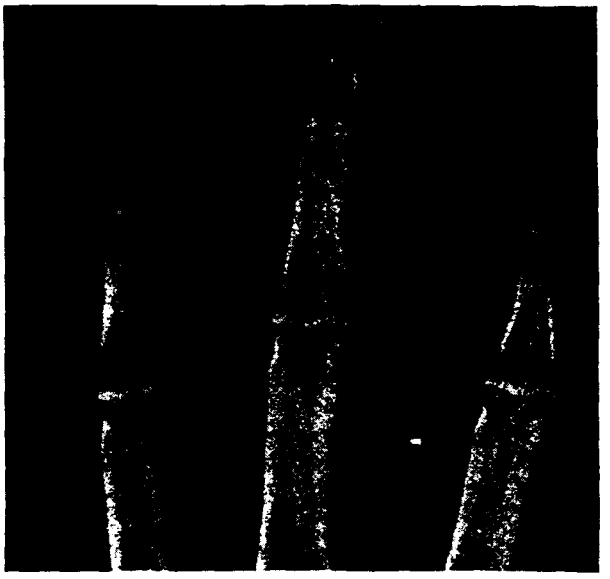
We have not observed any loss of calcium salt in the bones of the wrist and remaining bones of the hand and phalanges in any of these individuals, and there has been no evident sclerosis of the wrist and hand bones.

2. Mild stage: The earliest change found in acroosteolysis in these workers has been a loss of the cortex of one or more of the tufts of the distal phalanges, with no destruction of the tuft or shaft of the distal phalanx.

The next more advanced stage may be a small, half-moon cut in the cortex of the tuft of one or more

Table 1.—Summary of Symptoms and Findings

Symptoms	No. of Cases
Acroosteolysis without Raynaud's symptoms, one hand	4
Acroosteolysis without Raynaud's symptoms, both hands	5
Acroosteolysis with Raynaud's symptoms, one hand	5
Acroosteolysis with Raynaud's symptoms, both hands	17
Total	31
Clubbing of fingers	8
Skin nodules	8



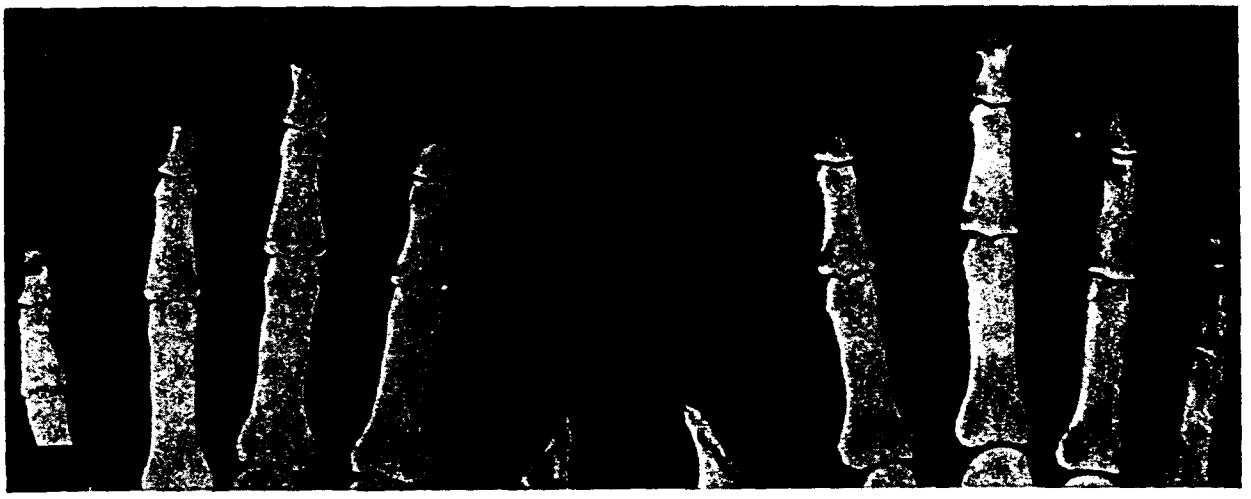
2. Mild stage of acroosteolysis with half-moon defect of distal phalanx of mid finger.

1. Acroosteolysis with involvement of distal phalanges of all fingers.

distal phalanges, or a so-called slice effect along one or more of the tufts. Figure 2 illustrates the small, half-moon cut in the cortex of the distal phalanx of the mid-finger.

3. Advanced stage: A more severe lytic destruction may be a complete loss of the tuft and a portion of the shaft of one or more distal phalanges as illustrated in Fig 1 in which the tuft of the distal phalanx of the right thumb and the tuft of the distal phalanx of the left fifth finger are completely absent. Additionally, there may be in the same hand a portion of the distal rim of the tuft remaining, with loss of the proximal portion of the tuft and a portion of the shaft of the phalanx, which can also be identified in the remaining phalanges in Fig 1. This loss may be of a transverse nature through the shaft and the tuft, or of an oblique type loss of bone structure.

4. Healing stage: In this phase, there is often definite fragmentation of the remaining tuft and of the filled-in area where the previous destruction was noted through the shaft of the distal phalanx. This may go on to a complete bony union or remain as a fibrous union with fragmentation. In Fig 3 and 4, x-ray films of the same individual well demonstrate this. This employee had almost complete reunion of the multiple fragments when first seen in November 1965 and again in November 1966 (Fig 3). In the latter, the completely healed shafts and tufts of the distal phalanges are indicated by no residual fragmentation with fibrous union. There is a definite shortening of the shaft and a widening of



3. *Above*, Acroosteolysis with marked fragmentation of distal phalanges in November 1965. *Below*, Same individual in November 1966.

the shaft and tuft, both in the transverse and the anteroposterior diameter. This is most likely due to a combination of constant pressure, and by the normal tension of the soft tissues, particularly the tendons to the distal phalanges.

Occupational Aspects of Syndrome

Based upon our observations of these 31 cases, it appears as if this syndrome may be of occupational origin and is somehow related to the process of vinyl chloride polymerization. Its specific cause if not presently known. We are performing extensive research in an effort to find the cause. Two other papers referring to the condition have appeared in the literature. The publication by Suciu et al[3] contains no specific information, and merely alludes to some hand problem. That of Cordier et al[4] presents case histories with symptoms similar to many of the cases we describe. This syndrome differs from idiopathic and familial acroosteolysis in that only the hands are involved.

Vinyl Chloride Polymerization Process

Polyvinyl chloride is a widely used synthetic resin. It has been manufactured commercially for more than 30 years and is used in upholstery fabric, floor and wall tile, wire insulation, phonograph records, and many other commonly used commodities. For many of these uses, the resin $(CH_2CHCl)_x$ is mixed with other materials to achieve the desired physical characteristics. The hand syndrome occurs apparently only in those people exposed to vinyl chloride or to other chemicals used in the manufacturing process of the resin itself or both. In addition to our examinations of 3,000 personnel performing vinyl chloride manufacturing and polymerization, we have examined more than 1,000 individuals who handle the finished resin or who process it into plastic products. *No cases of acroosteolysis have been found in these 1,000 persons.*

Table 2.—Age Distribution of Cases

Age Group	Acroosteolysis Without Raynaud's Symptoms	Acroosteolysis With Raynaud's Symptoms
20-29	1	4
30-39	4	12
40-49	4	6

Basically, the manufacture of polyvinyl chloride consists of polymerizing vinyl chloride. The reaction is accomplished in closed containers (polymerizers) with suitable catalysts and emulsifiers.

Copolymers, formed by combining vinyl chloride with other monomers, create variations of the homopolymer. These are commercially produced. Following polymerization, the resin is washed, dried, and sold as a finely divided white powder.

The polymerization operations are carried out in closed processes and provide little opportunity for employee exposure. Following the completion of the polymerization reaction, periodic cleaning of the walls and agitator of the polymerizer is necessary. The frequency of this cleaning and its method varies with the type of material used in these vessels and with different manufacturers. The most common practice has been to accomplish the cleaning manually by using hand scraping techniques, with workers spending several hours each day on this job assignment. Personnel performing this job are commonly referred to as "polycleaners."

4. *Left,* Healed acroosteolysis with only minor roentgenographic changes. *Right,* Same individual one month after crushing injury to midfinger.

Epidemiology

We have attempted to study the relationship of job history to the occurrence of the disease. Twenty-seven of our 31 cases have either been on the "polycleaner" job assignment at the time the syndrome appeared or have had that assignment at some time in the past. This job assignment is the only one showing any positive correlation with the occurrence of the syndrome.

Attack Rate.—The syndrome has a low attack rate. Our experience indicates it occurs only in less than 3% of all production employees who at one time have had polycleaning experience.

Age Distribution.—The youngest of our cases is 26 years old, and the oldest is 47, with the majority falling in the 30 to 39 age group. The complete distribution is shown in Table 2.

The appearance of the syndrome among younger employees may be influenced by the fact that the polycleaning job is one of the initial job assignments into which employees in such plants are hired.

Incubation Period.—If this syndrome is related to occupational factors, as we believe, then the time of exposure to these factors should be significant. We have investigated the time spent on polycleaning and, although accurate job-time assignment information is difficult to develop, it appears as if none of these cases has had less than 12 months polycleaning experience.

Comment

To our knowledge, this is a unique and, with the exception of references 3 and 4, previously unreported disorder. The specific cause is presently unknown, although it appears to be related to the manufacture of vinyl chloride and polyvinyl chloride. Not only are the x-ray findings of themselves unique, but when accompanied by the symptoms of Raynaud's phenomenon, the syndrome becomes extremely specific. As far as we are aware, this has not been an observed response to any toxicant in any of the animal species. We have attempted to arrive at an explanation of its cause, as well as the physiological mechanism whereby the extreme specificity for the distal phalanges of the hands occurs, but have been unsuccessful. We believe the condition is the result of three factors, all of which must be present for occurrence: (1) a chemical insult, (2) a physical insult, and (3) a personal idiosyncrasy. The chemical insult could occur from one or more of the monomers, catalysts, and intermediate reaction products existing in polymerizers. A low degree of exposure to these could occur from contact with the solid, slightly moist, residue in the polymerizer or to small quantities of vapor, absorbed either percutaneously or by inhalation. Research studies are in progress in an attempt to verify the chemical insult factor theory.

The physical insult is present in all "polycleaners" to some degree through the prolonged hand scraping operations as well as the occasional use of hammers to remove the residues. In support of the physical insult factor, we have quite recently observed the effects of a finger injury to an existing case of this syndrome. Figure 4 (*left*) shows an x-ray film of the left hand of the first of these cases of acroosteolysis (accompanied by Raynaud's symptoms and skin nodules on the dorsal surfaces of the hands). The bone damage is quite limited. Figure 4 (*right*) shows the same hand with the roentgenogram taken four months after a crushing injury to the mid finger, with lysis having resulted to the tuft of the distal phalanx. We believe this activity was stimulated by the trauma.

Personal idiosyncrasy appears to be an important factor because of the low incidence of occurrence of the disorder. This is especially significant because, although all polycleaners are subjected to essentially similar chemical and physical insults, the incidence of this syndrome is very low, and the explanation for this can only be made on the basis of personal idiosyncrasy. We suspect pertinent factors here are related to the individual's vascular system, the nerves controlling the blood supply to the fingers, and to the specific type of collagen in the individual's hands. We are in the process of investigating these factors.

We have observed no serious disability in any of these cases. A few have been partially disabled because of hand soreness, to the extent that some restriction in manual activity was necessary. Improvement in the symptoms, as well as in the roentgenological findings, has occurred in many cases without adequate explanation.

We wish to emphasize that no cases have been found, after extensive search, in individuals either working with the finished polyvinyl chloride or its copolymers, or in processing the polymer into plastic products. In these processes, more exposure to the polymer occurs than does in the manufacturing of the polymers themselves.

We presently believe that personnel assigned to polycleaning should be evaluated, prior to assignment, for any evidence of collagen disease, osteolysis of the hands, or abnormal response of the hands to cold insult. Any evidence of the existence of any of these factors should contraindicate the assignment of an individual to "polycleaning," and thus remove, or at least minimize, the personal idiosyncrasy factor.

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DEVELOPMENT CENTER

Central Technical File

19,700

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Date: September 12, 1967

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From: H. H. Marty
HHM-30-67

Status of PVC Task Force Activities

In our Task Force meetings, we have reported what activities are going on in various parts of the company. The following is an up-to-now report for the benefit of the Plant Managers and Technical Managers on studies we have been keeping an eye on.

1. Conversion Control

This is the most important single objective the Task Force has. No final decision has been reached as to the best method to use.

a) Louisville is still operating a single poly on the hydrofull method. Their results are still encouraging. The conversion of twelve polys to hydrofull operation is continuing.

b) Long Beach is waiting for delivery of a temperature integrator system so they can fully evaluate a ΔT approach. Initial results looked promising.

c) Long Beach has done further work on evaluating a system of early vinyl chloride removal. A pressure drop occurs in direct relation to the amount of vinyl chloride removed. For example, when 9000 lbs. of VCl are charged, & 1000 lbs. of VCl are removed toward the end of the polymerization, a pressure drop will occur at about 70% conversion. The effort now is on trying to determine the effect of rate of VCl removal, how predictable the method is, how consistent the results are and the effect upon properties. A production dried sample is to be sent to ALDC for examination of stability and other properties. A control will also be sent.

Henry was prepared to look at this method using two 3300-gallon polys for polymerization and two 4300-gallon polys for recovery. Increased production demands tabled their study.

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d) Avon Lake. Control of porosity has been erratic on both 102EP F-5 and 109EP F-2. This has forced a fine tooth comb analysis of all variables we can think of having an effect upon the process.

2. Air-Free Pearl Charges

In May, Henry completed a series of runs comparing air free and normal level air at hydrofull and normal charge sizes. The resin was 102EP F-5. Although it may require an effort to set up an experimental series (especially one statistically designed) and to complete the plant work, it takes far longer to get the resin tested and an evaluation made.

The major result obtained in the plant work was the observation that the hydrofull charges required two hours less to run to the desired porosity level than non-hydrofull charges. This was true for both the air-free and normal level air charges. Otherwise no process difference was noted.

The testing work is incomplete as of this date.

a) No difference in fisheyes was found using the Filmco test. John Whitney's lab tried several different extrusion conditions. But no significant change was detected.

b) The TOPS #37 evaluation by Warren Reed failed to show a difference between the materials tested. This test is used to evaluate heat stability characteristics of resin.

c) The Henry lab testing program is nearing completion.

d) The testing backlog was high for the Instron rheometer. Then it "broke down" for a time. To try to get an answer as soon as possible, we asked that only four samples be run. These included our two hydrofull lot samples, (air free and normal air level) and two which might have been the two extremes in the TOPS #37 test. Both of these were non-hydrofull charges; one was normal air level and the other was air-free. No difference was noted in the stability results in the four samples using the CVHE test.

e) George Baldrick used a 6461 recipe in evaluating the resin. It was hoped that this light colored compound would show up color or stability differences. Unfortunately the lead stabilizer (S-27) acted as an indicator for the BPA shortstop. As a result, the test lots were pink and dark. Now a darker compound will be used where the BPA-basic lead reaction will not be so obvious.

f) At the time of writing, we are not clear if Jack Quint, ALDC, will extrude wire to see if this will pick up differences.

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3. Productivity of Hydrofull Approach vs. Long Beach Method

For several months a study of the productivity of the hydrofull process and of the so-called Long Beach method has inched along. When first initiated at the end of March, the two methods were of the same productivity. The basis for hydrofull production was 3300-gallon polys using IPP catalyst. The Long Beach basis was 2550 gallon polys using lauroyl peroxide catalyst and top recovery of VCl.

Now the Long Beach productivity is based upon IPP catalyst. This condition finds Long Beach productivity being better than the Henry hydrofull productivity. The report comparing the two routes is scheduled for issuance at the end of September.

4. Air-Free Paste

The oxygen analyzer was checked out. At present a wiring change in the instrument prevents use of the high range of our dual range capability. We can cover multiple ranges with the range cards we have now. These cards are 0-10/0-10,000 ppm O_2; 0-10/0-100 ppm O_2; 0-100/0-1,000 ppm O_2. So we can go from 0-10 up to 10,000 ppm O_2. We can use the instrument for batch or continuous measurement.

With the instrument so close to being used as a monitor, the air-free paste study was not started. It is now being started. The studies cover five variables - head peaking, temperature, catalyst (IPP) level, oxygen scavenger (sodium hydrosulfite) and oxygen level. The Ohmart gauge is being used in this study.

5. Heat Transfer Measurements

No experiments have been run on Poly 113 since June. In the first two series, large errors were found between heat input and output. The errors were of 200 to 250% magnitude. Since the flow meter for the water was believed to be the cause of error, it was decided to reactivate the orifice in the recirculation line as a check on the magnetic flow meter. This is now done. We also plan to calibrate the two resistance bulbs, used to measure ΔT in the jacket (T out-T in), for accuracy or consistency. If the differences between the bulb readings is not correct, our BTU determination certainly will be in error.

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6. Catalysts

a) Louisville looked at Lucidol IPP.

On pearl they saw no difference in reaction rate, the product properties were within specification and the catalyst was easier to handle.

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On the latter point, the IPP is supplied in a disposable plastic tray. The catalyst can be popped out frost free, ready to mix with the hexane. Five paste charges were made. The reaction rate might have been slightly slower (0.1 hour) but this could be due to a difference in catalyst concentration.

b) Henry worked with Lupersol 225 (di-sec lentyl peroxy dicarbonate).

Lupersol 225 is easier to handle (liquid) and has better solubility in hexane. This catalyst was charged in 102EP F-5 and 103EP F-72. No difference in reactivity or action was found when making either resin. Samples of each test resin and of IPP control resins were sent to ALDC for evaluation.

c) Niagara Falls tested Lupersol 11 (t-butyl peroxy pivilate) and Alperox C (lauroyl peroxide).

There is no recommendation to use Alperox C in 202 manufacture - the cost runs higher, the reaction is slower.

Lupersol 11 - started reaction quickly, produced even polymerization, died at end of polymerization, the reaction time was longer than for caparylyl. The resin (202) was in spec.

d) Long Beach is taking a while to get over on IPP. An E.A. was written to install the catalyst injection system. The IPP/hexane solution will be added thru the seal addition line.

7. Shortstops

Research recommended thiocarbanilide (TCA) as a shortstop for VCl polymerization. An initial test series was completed on 102EP F-5 resin. 1100-gallon polys were used with the hydrofull technique. A charge in one hydrofull poly was shortstopped with TCA and one in the second poly was shortstopped with the regular amount of BPA. The TCA addition was made at three levels. First an amount equivalent to the molar concentration of catalyst originally charged, then at one-half the catalyst weight charged and third at one-fourth of the catalyst weight charged. The heat stability of the products shortstopped with TCA was equivalent to that of BPA shortstopped resin. This was found on the Ba-Cd-Zn test. TCA was a more effective shortstop than BPA but, in the tests run, it did not stop the polymerization completely.

The series will be repeated. Injection water will be kept on during a six hour holding period for both BPA and TCA shortstopped charges. The water addition rate will serve as a good indication of how effective the shortstop is. Samples will be taken at shortstop and 6 hours after shortstopping.

At Research, a mixed BPA-TCA shortstop produced a product stability equivalent to that of either shortstop when used individually.

A single Geon 124 charge (15 gallon size) was made and 0.01 parts of sodium borohydride was added. There was no substantial shortstopping effect, as such. However, there was an improvement in product heat stability that was greater than for BPA. This is worth following further. Concentration must be reduced or the effect must be outstanding to balance the cost of the material.

8. Dynatrol Viscometer

A box was constructed to house the Dynatrol probe inside Poly 112. For a time, leaks shorted the instruments. This was corrected. After a couple charges, the probe was damaged during cleaning. A new probe has arrived. It is to be installed again.

We are trying to measure the viscosity profile of a pearl polymerization. The Dynatrol has given an indication of this profile. But to date we don't know how reproducible the instrument is and how much individual charges vary. Care is required in handling the viscosity proble. Today I doubt that it will be used for more than experimental studies - though they are an important aspect of this work.

9. Blowdown Tank vs. No Blowdown Tank Study

An analysis of costs and process advantages of a plant with blowdown tanks and of one with no blowdown tanks has been completed. The advantages of the Long Beach design were reviewed at Henry with G. D. Schaaf and H. W. Long taking part. The preliminary costs were examined by Long Beach and Henry people. A report is ready to be issued now.

For a 60 million pounds/year plant, a no blowdown tank plant costs $130,000 less than a blowdown tank plant. More storage space for slurry, recovery and carry over was provided. One point to watch is that provisions are made to provide for a hydrofull system if we employ this route.

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10. Agitation Studies

Various agitation equations are being put into a computer program for the Cleveland computer. The plan is to write the program(s) so they can be available via teletype terminals. In this way men in the plants can use the system. Design and process charges will be more easily accomplished in the future.

Long Beach examined the effect of slower speed agitation upon resin quality. This was done in trying to solve a particle size problem for Anaconda. The

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speeds studied were 60, 75, and 95 rpm. The 60 rpm speed gave buckshot particle size. The 70 rpm level produced 26% on a 60 mesh screen though the flow time was fast. The 95 rpm material had a very small amount of both coarse particles and fines and its flow time was better than normal production.

11. Math Model of the Pearl Polymerization Process

The development of a math model is being approached from two angles. A. T. Schooley and P. Y. Adams of the Research Center went through an analysis of the data available, the necessary efforts to write a model and the expected outcome. Due to the complexity of the model, about two man years would be needed to rough out a model and two more man years for checking it out and polishing it.

Dr. S. I. Cheng is attempting to construct a model. He has given the problem considerable thought over the last year. On September 20 he is to present his method of developing a model and the reasoning involved in his approach.

12. Clean Poly Studies

The data from 110 - 15 gallon Geon 700 charges are being statistically examined. About one-third of the time the poly was as clean after a charge as it was initially. This study is expected to shed a light on what causes the reactor wall to become dirty or to remain clean.

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