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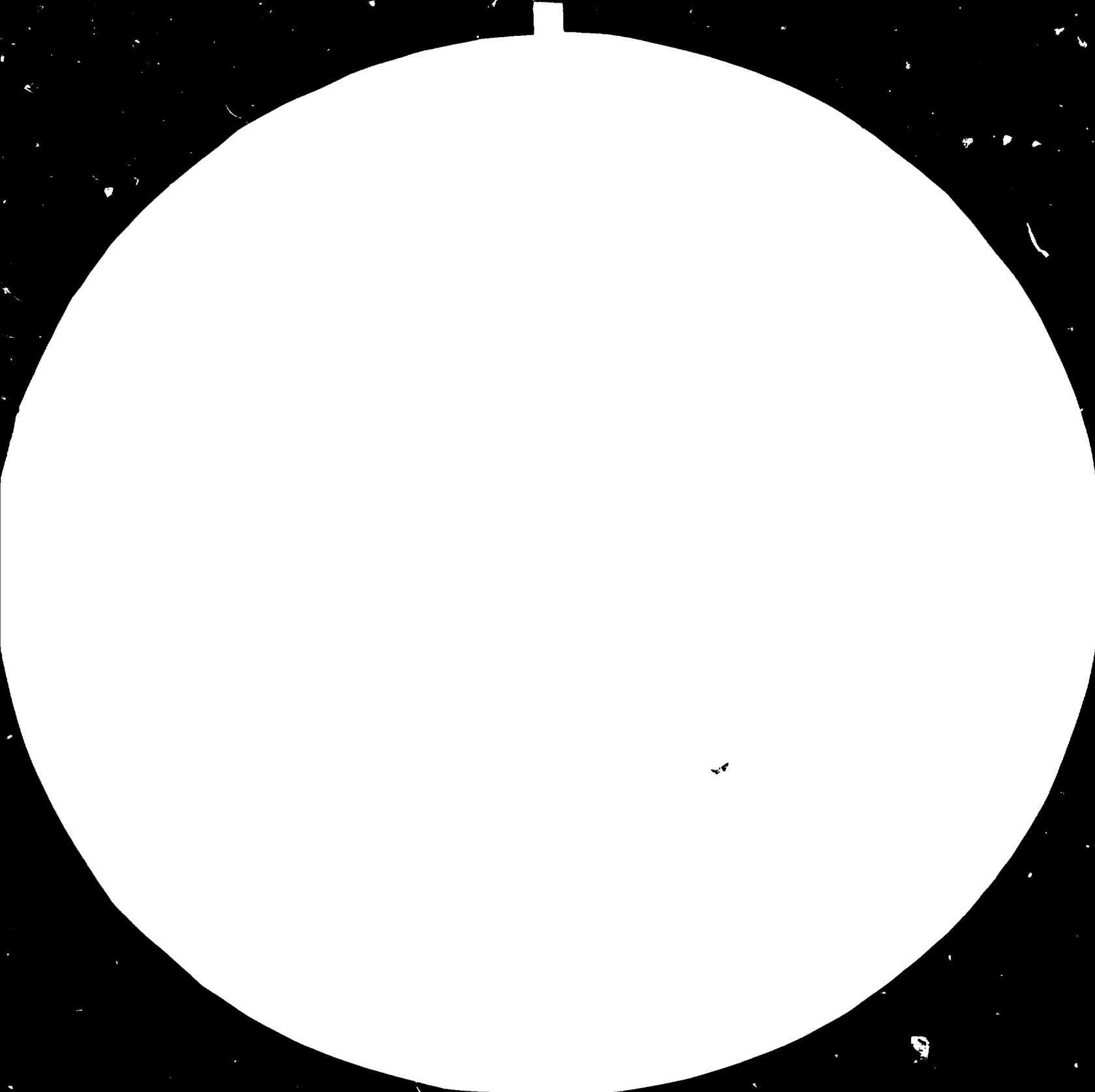

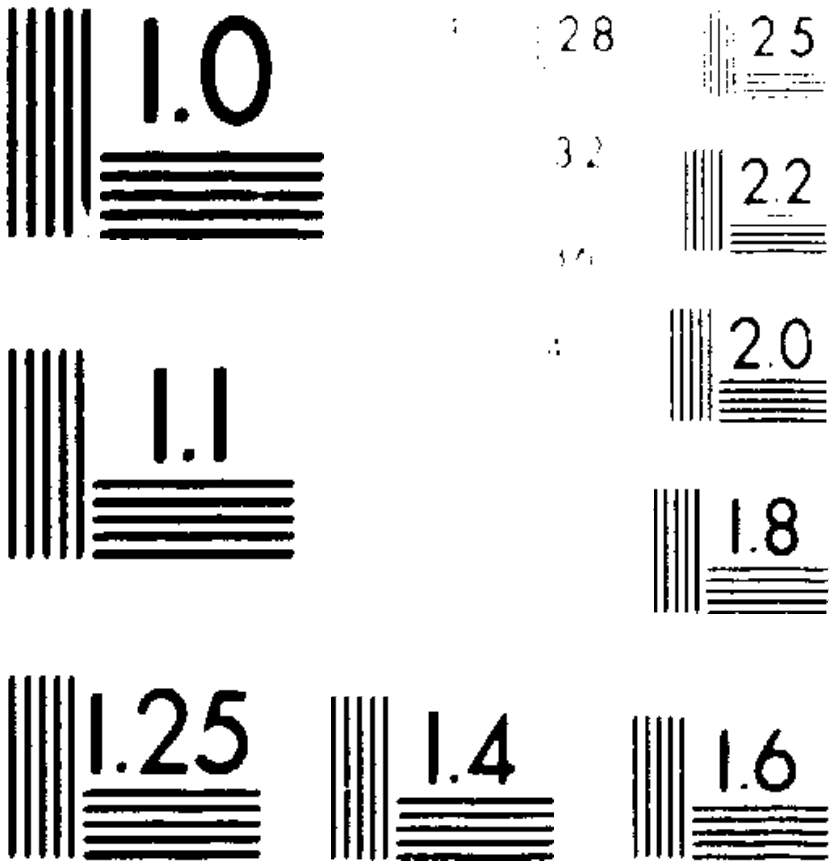

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16 April 1984

English

DPR of Korea.

PVC polymerization

SI/DRK/83/802/11-01/32.1.H

Democratic People's Republic of Korea

Final report

is prepared to the Government of DPRK

UNDP and UNIDO

(mission 5 march-16 april 1984)

Based on the work of Shamil Vezirov,

expert UNIDO in the field of PVC po-

lymerization

CONTENT

## 1. Summary

Duriug expert's, Mr. Vezirov, mission at IHMC, Hamhung DPRK (period 5 march-16 april 1984) the detailed acquiantance with research directions in the field of PVC production was carried out. The everyday discussions with laboratory staff gave opportunity to find out the main problem in that field, and particularly, low thermostability of polyvinylchloride.

The analysis of to-days situation gave possibility to work out measures directed to part improvement of polymer characteristics, by changing of technological parameters, method of experiments etc,

In close collaboration with the laboratory scientists complex programme on PVC problem was outlined, which based on the more detailed studying of polymer structure and its influence on the physico-chemical properties of polyproducts, and consultations with specialists in the field of preparation and processing of PVC.

On the 16th april the programme on the "PVC polymerization" was completely finished.

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## 2. INTRODUCTION

My activity as a UNIDO expert corresponded to the job description and work programme which was completely finished.

The mission on PVC polymerization at the Institute of High Molecular Compounds (IHMC) was begun on the 5th of March after finishing the work on the "Catalyst Research and Development for Industrial Applications" project.

During the period 5-13 march through the talks with the IHMC deputy director dr. Bong Sen Ha and heads of laboratoreies I was acquainted with the structure of Institute, main research directions and IHMC connections with DPRK industry. Several discussions took place with the staff involved into PVC production which gave possibility to find out their main problems, and particularly, low PVC thermostability, processing difficulties.

The situation concerning the purchase of equipment and sending fellowship abroad was also examined.

The same period on the base of discussion results the work programme was worked out and sent to UNIDO (see Annex 1).

All above mentioned was discussed in UNDP, Pyongyang on the 11-13 of march, where I also submitted the prepared final draft project on catalyst researches.

On the 14th of march I continued the work at IHMC analysing the research being carried out by separate groups

of vinylchloride polymerization laboratory, and particularly: Vinylchloride synthesis, initiator preparation, vinylchloride polymerization and its copolymerization with vinyldenechloride.

Every-day discussions with IHMC deputy director and other scientists gave me possibility to outline the measures which must be done for partly improvement of PVC quality with the existing facilities, as for instance, changing of some technological parameters, order of catalytic component injection into reactor, choice of new catalytic system etc.

At the same time together with IHMC staff the complex programme of PVC solvation problem was worked out. One of the main restricting factor in this way is absence of necessary modern equipment. Such a fact gives small possibility to determine and characterize the structure of polymer and its influence on the physico-chemical properties of final product.

The list of necessary equipment is given in Annex 2.

More deep and expand studying of the process with modern instruments demands also to improve the skill of laboratory staff, therefore the invitation of specialists on this problem as well as sending fellowship abrodd would be very desirable. Consultant's concrete fields are shown in Annex 3.

After dicussions with IHMC deputy director a perspective research plan on this problem was worked out which included:

To continue the investigations on PVC polymerization problem, paying attention on improving the indexes of vinylchloride synthesis stage. Particularly to use the modified catalyst, change some technological parameters. To expand research on studying the infleuence of polymer structure on the physico-chemical properties, which can be considered as a precondition for improvement of the thermostability, temperature characteristics, impact hardness as well as to escape the "eye-fish" phenomenon.

To use some new catalytic systems to achieve the uniform rate of polymerization. To involve new monomers, as acrylonitrile, olefins in copolymerization reaction with vinylchloride.

The new semiplant unit must be constructed this year for PVC-processing where the laboratory results will be tested. Taking all this into the consideration the IHMC plans to extend their staff by admission of 5 people for vinylchloride polymerization laboratory and 15 for PVC processing.

During the period of my mission at IHMC I delivered five lectures on the next subjects:

1. World tendency in PVC polymerization.
2. Methods of vinylchloride synthesis.
3. Radical polymerization of some substitute ethylenes.
4. New directions in vinylchloride polymerization.
5. Choice of comonomer in vinylchloride copolymerization reaction.

The programme on the PVC polymerization problem was completely finished on the 16th of april.

## 3. SELECTED AREAS OF RESEARCH AT IHMC

The Institute of High Molecular Compounds(IHMC) was established in 1960 within the academy of sciences located in Hamhung. The total Institute staff is 250,of which 110 are scientists with PhD, post graduates and graduates. The Institute includes 8 laboratories and organized along the following lines:

Laboratory 1- PVC synthesis by syspension or emulsion polymerization.

Laboratory 2- Synthesis of polymers with insulation properties and polyimides.

Laboratory 3-.PVC and PE processing laboratories.

Laboratory 4- Laboratory of Vinalon quality improving

Laboratory 5- Synthesis of PVC fibres.

Laboratory 6- Rubber synthesis on the base of chloroprene and calcium carbide.

Laboratory 7- Rubber processing laboratory.

Laboratory 8- Synthesis of suspended dye materials.

Two semiplant units at February 8 Vinalon complex in Hamhung are used for testing polychloroprene and Vinalon processes.

The problem of PVC production has the vital importance in the sense of satisfaction the industry and agriculture of DPRK with the polymer materials with valuable properties. At present time polyvinylcloride is one of main plastic polymers produced in different countries because of its some outstanding physico-chemical properties.

Oil and gas are the main natural sources usually used for that purpose. DPRK has no such kind of sources and therefore anthracite as an alternative raw material is used now in PVC production.

4. RESEARCH DIRECTIONS AT PVC POLYMERIZATION LABORATORY

Taking into consideration the rather rich sources of anthracite and demands of country in plastic polymers the staff of PVC polymerization laboratory IHMC are now involved with the next main project.

1. The catalyst synthesis for vinylchloride production.
2. The synthesis of vinylchloride by using the acetylene method.
3. Vinylchloride polymerization.
4. Vinylidenchloride-vinylchloride copolymer synthesis.

Technology of PVC production consists of next stages; synthesis of calcium carbide from anthracite, synthesis of acetylene from calcium carbide, synthesis of vinylcloride on the base of acetylene and hydrogen chloride gas, vinylchloride polymerization.

4.1 Catalyst preparation for vinylchloride synthesis:

The stage of catalyst preparation is carried out according to the industrial method of coal activation by chemical reagent at the Vinalon complex. The preparation consists of pressing the mixture of wood sawdust and $ZnCl_2$ with further cutting to 4mm tablets. After keeping the tablets at 450-500° under the nitrogen atmosphere they are immersed into the water for salt dissolving.

The obtained porous coal has 800-1000$m^2/g$ average surface. Its activation is achieved in the mercury chloride solution at 40° during 1 hour, Such industrial catalyst requires some modifications.

It has to be improved because of unsatisfactory life-time (not more than 6 months) and low mechanical hardness.

The last, as well as resin forming during reaction process considerably decreases the process indexes.

Taking in to consideration the above said, the laboratory is beginning now the research on the catalyst problem, particularly, using the vacuum laboratory unit for catalyst surface determing and studying its influence on the activity.

Initiators: Research work in initiator preparation in DPRK began in 1958 before Vinalon complex was put into operation, Azobisisobutyronitrile (AIBN) was the first initiator for suspension polymerization wich was synthesised from acetone, hydrazine, HCN and chlorine. Showing rather good stability such initiator wasn't active in Vinylchloride polymerization, the same as synthesized later in 1960 benzoylperoxide.

Trying to find more active compound laboratory of IHMC synthesized a new initiator-azobis-2,4-dimethylvaleronitrile on the base of diacetone alcohol; Activity of new initiator was 3 times higher than AIBN.

Institute continued the research work in finding the appropriate initiator for vinylchloride polymerization.

The new object of researches was synthesis of peroxidicarbonates and, particularly, diisopropylperoxidicarbonate (IPP). The last was obtained by known method on the base of isopropylalchohol, phosgene and $Na_2O_2$.

This initiator showed high activity in polymerization but wasn't stable at room temperature, requiring its storage at-10°. The present time laboratory has some experience in vinylchloride polymerization using the mixture of AIBN and IPP. The aim is to increase the polymerization speed at the initial stage. The obtained results gave possibility to recommend it for industry and now Vinalon complex is using this recommendations in PVC production.

Vinylchloride synthesis: Vinylchloride synthesis is carried out in flow tube column reactor in the presence of fixed bed above mentioned catalyst by passing of acetylene and hydrogen chloride at 150°-200°; conversion of the initial components at the chosen parameters is about 95.0% , reaction selectivity 95-97%.

After further low temperature rectification the monomer purity achieves 99.9% and it can be used for polymerization. Mercury sublimation as well as corrosion problem are the main negative factors at this stage which can be solved by changing of process technology and using of appropriate catalyst.

4.2 Vinylchloride polymerization: The laboratory investigates two types of vinylchloride polymerization, studying the suspension and emulsion methods. The suspension polymerization is carried out in periodical 5 lt apparatus, at 50° temperature, pressure of vinylchloride vapours 8.0 atm, duration 12 hours, using azo-compounds as initiators. The loading of polymerizator is realized in turn by adding at room temperature and agitation of demineralized (distilled) water, polyvinylalchohol as a stabilizer, vinylchloride-initiator mixture. By heating, the reaction temperature-50°is achived in 30 minutes. At such a condition monomer conversion after 12 hours is about 80.0-90.0%.

Up to date only primary characterization of obtained PVC samples is determined and among them glass transition temperature 80°, thermostability (HCl educing) -165°. The experiments using age oven showed that prepared PVC film can work ; about 1 year in field conditions. Addition of some stabilizers such as 2,4-dihydrobenzophenon, phosphites, Ba-stearates increased their life-time up to .5 years.

Laboratory has some experience in emulsion polymerization of vinylchloride using the same experemental apparatus. This reaction is carried out at the experimental conditions: temperature 45-60°, duration 20 hours, pressure of vinylchloride vapours 5-6 atm. The components of catalytic mixture are added at next order: water-emulsifier-Ph regulator-initiator-monomer. Checking different initiators as ammonium persulphate, kalium persulphate, $H_2O_2$ the first one was chosen as more preferable.

Laboratory studied polymerization process in the presence of different emulgators, among them Na-sulphate laurile, which is now not producing in the country, some surface-active substances (OP-10,OS-20) and alkylsulfonates.

The last one was synthesized in the Institute of organic chemistry AS DPRK on the base of $C_{11}$-C18 hydrocarbons, $SO_2$ and chlorine with further soponification obtained alkylsulphurchloride.

Such compound now is produced in the country and found its application in emulsion polymerization.

The achieved vinylchloride conversion in experiments was about 80.0%. Emulsion particles had the sizes 1000A.

Trying to improve the latex stability, research in seed polymerization of vinylchloride was begun. Two methods of such polymerization were studied.

According to the first one the latex was injected into the reactor before polymerization. In the second case portion injection had place. The most important problem was to find out the optimal speed of such injection, which was solved by laboratory research group. The obtained latex was more stable with particle sizes 2500A.

4.3 Vinylchloride copolymerization: The same techniques are used in laboratory for vinylidenchloride-vinylchroride copolymer preparation. The suspension copolymerization is carried out in the presence of azo-compounds, temperature 55°, weight ratio vinylidenechloride-vinylchloride-70:30, pressure of vinylchloride vapour-3,5atm, duration 50-60 hours, The calculated amount of vinylidene chloride is added to distilled water at room temperature and at continual stirring mixture vinylchloride-initiator is introduced through the input on the cover of reactor. Up to-date conversion achieves 70.0% which does not satisfy the research group involved in

that problem. The reason of slow reaction speed propar- is the forming of nonactive macroradical at the propagation stage. The ratio of monomer links in obtained copolymer vinylidenechloride: vinylchloride-85:15.

4.4 Physico-chemical analysis of (co)polymers:

Some primary characterization of polymer products occurs now in laboratory No1 and particularly:

- Suspension sizes are determining by using photocalorimetric method.
- The polymer density is defined by immersing of polymer films into $ZnCl_2$-water solution.
- The content of chlorine in polymer by means of electric charge burning of samples and next hidrogene chloride adsorbtion by $Na_2Co_3$ for further titration.
- Viscosity data gives the approximate notion about molecular weight of prepared polymers.
- Polymer decomposition temperature is determinied by heating of samples with further fixing of educed HCl by caustic soda for titration.

The other laboratory which is involved in PVC problem researches the polymer processing. The laboratory staff is 23 (head of lab,-1, scientists with PhD-3, scientific workers-10, laboratory assistants-9).

The laboratory has some equipment for studying the polymer physico-chemical properties as: glass transition temperature, hardness (Hungarian instrument), stretching, compression, impact hardness, influence of IR and UV-rays on the polymers films. Age oven (max temperature 200°, Japan) gives some data about the polymer thermostability.

## 5. IHMC COLLABORATIONS WITH INDUSTRY

IHMC had close connections with some industrial plants, located in DPRK. During my stay I have visited several plants where the Institute suggestions were used for industrial application:

- At present time at vinalon complex 90% of PVC production is produced using the suspension method and only 10% by emulsion polymerization. But in near future the industry plans to increase the percent of emulsion PVC to get more large amount of paste polyvinylchloride. The total capacity of PVC polymerization unit now is 50th.t/year.

Besides the main unit there are two small apparatus 40$\ell_t$. volume where the IHMC researches periodically check the findings of their experiments with further suggestion to the plant.

-At the PVC processing plant in Hamhung where the total staff is 2000 there is an equipment to produce the plastizied polyvinylchloride. The capacity of the last is 6th t/year. The plant uses such additions as dioctylphthalate, dioctiladipinate, dibutylphtalate.

The processing temperature is 170° The obtained PVC film is used further on the spot for producing raincoats, wall-papers, bags, toys etc.

The IHMC helps this plant giving suggestion on the recipe of additions using ; particularly advice on the 2,4-oxybenzophenone compound to protect UV-rays. The plant gets periodical consultations of IHMC scientists.

-Nam-Hung petrochemical complex which is located 120 Km from Pyongyang produces polymer products as polyacrylonitrile fibres, polyethylene as well as chemical fertilizers and different chemicals.

At present time the plant uses mainly the imported equipment from France, Romania, Austria as well as technology, but some industrial apparatus is made in DPRK. IHMC, studying the technology of copolymers production suggested to change some polymerization parameters to improve the quality of final products, their assistance was also in testing of physico-chemical properties of obtained polymers.

In future research collaboration IHMC plans to involve the butadiene which is working out at the plant in naphta pyrolysis process into the copolymerization reaction with acrylonitrile for its further industrial realization at the same plant.

Besides that a new addition on the base of sulphur compound for lubricants, produced at Nam-Hung complex which increases the stability and UV-resistance is now studying to substitute the now days using "ionol" for that purpose, but imported from abroad.

## 6. FINDINGS

At present time the laboratory of IHMC studying the PVC polymerization has problems concerning the improvment of polymer thermostability and PVC processing.

The existing equipment for estimating the physico-chemical properties as well as the structure of polymers gives possibility to make a conclusion only about the approximate character of obtained final polyproducts, The problems can be solved:

1) By changing of some technological parameters, catalytic system and experimental methods of PVC preparation, studying the kinetic of polymerization as well as decomposition reactions. All such measures can be carried out on the existing equipment.

2) Taking into consideration the considerable influence of polymer structure on the physico-chemical properties to use the modern corresponding instruments (list of instruments is shown in Annex 2) to obtain the necessary data for their interpretation.

## 7. Recommendations.

Quick solving of the above mentioned problems requires:

- To change the technical base of PVC polymerization laboratory supplying it with modern laboratory units and instruments.
- To expand the staff working on all stages of PVC production.
- To develop research in complex studying of active coal-mercuric chloride catalyst (preparation method, structure and its influence on activity etc) to improve its mechanical property as well as catalyst life.
- Using the existing facilities the quality of polyproducts can be partly improved by a) changing of some process parameters, particularly, order of componets addition, b) prereaction heating of distilled water to escape the begining of polymerization at low temperatures, c) changing (decreasing) of final conversion degree
- To check some other catalytic systems used for PVC polymerization as redox system, metal salts, metal carboniles, halogen substituted carbons etc, for carrying out the polymerization process at low temperatures; the last provides forming of more stereoregular polymers with high thermostability.
- To use as a component of reaction mixture special additions to prevent the forming " fish eye" structure , as esters of unsaturated fat acids.

- To purchase the modern equipment for studying the physico-chemical properties and structure of polymers(list of equipment see Annex 2)
- To improve the skill of laboratories staff it is desirable to organize the fellowship practice abroad in the countries which have PVC industrial scale application (Austria, USSR, GDR)
- To develop research on the kinetic measurments of polymerization reaction as well as decomposition of PVC
- Taking into consideration that according to the project budget the sum about 3000$can be used more for instruments purchase hardometer, 2 lt autoclave (100 atm pressure), high seusitive recorder, ultra-thermostate.
- The solving of PVC polymerization problems needs consultations of experts (more in detail see Annex 3)

INSTITUTE of High Molecular Compounds AS DPRK

Work programme in PVC polymerization problem during the UNIDO expert Sh. Vezirov mission (period 5 March-16 April 1984)

SI/DRK/82/11-01/32.1.H.

Work plan is working out according to the job description of UNIDO expert and after discussion of PVC polymerization problem with deputy director of IHMC and heads of laboratories. The expert's work in IHMC started on the 5th of March 1984 in collaboration with institutes staff. The work plan which was settled out during the first week of experts staying in IHMC isshown below.

Period 5-13 March

a) Acquaintance with the structure of IHMC and particularly with the laboratories involved into PVC polymerization problem.

b) Working out of work programme on this problem with the IHMC counterpart specialists.

c) Definition of several project problems concerning the equipment purchase, sending of fellowship etc. for their discussion and solution in UNDP.

d) The discussion of above mentioned in UNDP.

Period 14-21 March

- Detailed acquaintance with research work in the field of vinylchloride synthesis which includes:

1) Method of initial compounds as well as reaction products analysis.

2) Laboratory units for carrying out the vinylchloride synthesis.

3) Methods of monomer preparation and experiment conditions to achieve an appropriate yield.

4) Discussion with laboratory staff on the research work and recommendations.

5) Lecture concerning the world tendencies in PVC production.

Period 22-28

Detailed acquaintance with investigations in the field of initiators preparation which includes:

1) Acquaintance with the method of initiator preparation and its storage.

2) Analytical control methods of initiator purity, impurity content definition.

3) Methods of characterization of initiator and method of investigation on its decay and activity.

4) Discussion of observations with the counterpart staff.

5) Experts lecture on the methods of PVC synthesis.

Period 29 March-4 April.

Detailed acquaintance with the research in the field of PVC polymerization which includes:

1) Acquaintance with methods of PVC polymerization.

2) Observation of polymerization reaction, which means the choice of initiator, medium, experimental conditions etc.

3) Acquaintance with the characterization methods of obtained polymer.

4) Discussions with scientists on that problem and recommendations.

5) Expert lecture on the PVC polymerization problem.

Period 5-11 April.

Detailed acquaintance with the investigations on the PVC copolymerization, which includes:

1) Selection of comonomer for studied reaction.

2) Experimental conditions in copolymerization reaction and their influence on the properties of final polyproduct.

3) Characterization of copolymer products.

4) Discussion with laboratory staff on that problem.

Period 12-15 April.

Preparation of final report on the base of findings, setting out recommendations to the Government.

April 16.

Discussion of expert's mission results in UNDP.

April 17.

Departure from Pyongyang.

On behalf of IHMC AS DPRK

Scientific assistant Director

Bong Sen Ha

Sign: 봉선하

On behalf of experts of UNIDO Representative

Vezirov Shamil Suleiman ogly

Sign:

March 10, 1984.

9. Annex 2

Equipment required in PVC polymerization project

| | Quantity | Cost, US $ |
|---|---|---|
| 1. Infrared spectrophotometer | 1 | 16000 |
| 2. Gel-chromatograph | 1 | |
| 3. Light scattering photometer | 1 | |
| 4. Differential therm analyzer | 1 | |
| 5. Hardometer | 1 | 500 |
| 6. X-ray difractometer | 1 | |
| 7. Osmometer | 1 | |
| 8. 2 liter autoclave (100 atm. pressure) | 1 | |
| 9, Conductometer | 1 | |
| 10. High sensitive recorder | 1 | |
| 11. Ultra thermostate | 1 | |

10. Annex

Consultants required on PVC polymerization project.

1. Consultant in preparation and characterization of active coal catalysts, studying their activity and selectivity in acetylene hydrochlorination reaction

2. Consultant in the field of kinetic measurments of polymerization as well as decomposition reactions, their further interpretation for understanding the mechanism of studying processes.

3. Consultant in the field of PVC (co)polymers estimation, with the experience in studying the different physico-chemical methods of structure definition (porous, degree of crystalinity etc) using modern instruments.

## 11. Acknowledgment

I should like to thank the Government of DPRK, project authorities for their efforts and attention which I felt during all my stay at IHMC. I also appreciate to IHMC deputy director dr. Bong Sen Ha and PVC laboratory staff for their help and participation in my work.

I thank members UNIDO chemical Industries Branch and UNDP members for assistance on the project.

Expert UNIDO / Sh. Vezirov/