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ASSISTANCE IN THE PRODUCTION
OF DYESTUFFS

SI/DRK/84/803

DEMOCRATIC PEOPLE'S REPUBLIC OF KOREA

14836

D.P.R. Korea.

Technical report: Development of new grades of deep colour dyestuffs
for polyvinyl alcohol and nylon .

Prepared for the Government of the Democratic People's Republic of Korea
by the United Nations Industrial Development Organization
acting as executing agency for the United Nations Development Programme

Based on the work of Hassan S. Mahmoud, expert
in the research and development of dyestuffs

United Nations Industrial Development Organization
Vienna

3622

This report has not been cleared with the United Nations Industrial Development
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ABSTRACT

Under the Project SI/DRK/84/80³ Assistance in the Production of Dye-stuffs; lectures, a seminar, laboratory experiments and field visits were carried out in co-operation with The Institute of Organic Chemistry, Academy of Science Branch at Hamhung.

Subjects and activities:

- Two lectures and one seminar were presented dealing with dyestuff research work, especially on 1:2 chromium complex dyestuffs.
- Review of the existing laboratory facilities.
- Improving existing techniques for the preparation of bluish black 1:2 neutral chromium complex dyestuffs.
- Visits to the existing facilities in the industrial production of dyestuffs and textile mills.

Conclusions and recommendations:

- The main textile material in the country is Vinalon (polyvinyl alcohol). The country's intention is to replace imported dyestuffs with local production.
- Research on dyestuff is considered as organic synthesis only.
- Industrial production units are very old and lacking modern techniques of product finishing and quality control.
- It is recommended to modernize research laboratories and equip them with necessary instruments for dyestuff evaluation (colour testing). The research staff should be trained in the field of application and evaluation of various types of dyestuffs.
- It is recommended to redesign and modernize completely the dyestuffs' production facilities through a technical assistance programme.

INTRODUCTION

A. Mission schedule

The expert arrived in Pyong Yang on 6/5/85 by noon and contacted the UNDP office the same day. The resident representative, Mr. Ristic, was absent. An introductory meeting was held with Mr. Yong Tu Long, the deputy resident representative, and Mr. Li Song U, the back-stopping officer of the project.

Next day a working plan was discussed with the representatives of Academy of Science--Mr. Kim Hyon Ki and Mr. Li hang il.

On 8/5/85 the group travelled by train to Hamhung, 400 km , north-east of Pyong Yang to the Institute of Organic Chemistry.

9/5 - 21/5/85

Execution of the mission's work programme at the Institute of Organic Chemistry, Academy of Science branch (Hamhung).

It was declared that the expert's main task should be to advise on the preparation of dyes for vinalon. He examined the present facilities at dyestuffs laboratories and reviewed the technologies applied. Advice was given on the diazotisation with nitrosyl sulphuric acid, chromium complex formation using chromium salicylate complex. The expert demonstrated laboratory trials to prepare deep colour of neutral 1:2 chromium complex dyestuff. The work carried out by the expert at the Institute fulfilled completely the immediate objectives of the project. It covers the items (d) and (e) of Section (f) Activities of the project document.

Two lectures and one seminar were held with the participation of research staff of the dyestuff laboratory and some representatives of dyestuffs manufacturing plants.

-----Field visits were paid to Hamhung chemical complex where vinalon is being manufactured. The expert reviewed the dyestuffs production units and pilot plant.

22/5 - 27/5/85

-----Field visits to textile mills in Hamhung and Pyong Yang were carried out to investigate the dyeing procedures of vinalon and the existing dyeing equipment.

B. Recommendations

1. The dyestuff production industry is obsolete as regards both machinery and techniques. The results of laboratory research, even if expected to be good, will not be of commercial value for industrial application due to the present state of the industry. Technical assistance should urgently be rendered either through UNIDO or by bilateral agreements under the umbrella of UNDP. The assistance programme should be executed by a team of experts and cover: establishment and start-up of dyestuffs plants, dyestuff quality control, finishing and standardization of dyestuffs, and synthesis and developments of dyestuffs suitable for the Korean textile industry. It is highly recommended to prepare a pertinent Assistance Project (UNIDO, Government).
2. Training of technical staff on the evaluation and application of dyestuffs. (UNIDO)
3. Modernization of the dyestuff research laboratories which need to be equipped with dyeing and fastness test apparatuses to evaluate precisely the obtained research data. (Government)
4. Modernization of the dyestuffs production units which need to be equipped with all the necessary quality control facilities and machinery for finishing and standardization techniques. (Government)

I. ACTIVITIES

A. Review of the technology and processes presently applied for dyestuff production

1. The technology followed in the dyestuff research laboratories of the Institute of Organic Chemistry, was based mainly on data published in literature. The purpose of applying the research results in industry was not taken into consideration. As an example, the 1:2 chromium complex azo dye was prepared by chromating the azo dye with chromium salt in ethylene glycol. This method is one of many data present in literature, but has no useful commercial application. The expert advised use of the chromium salicylate complex. Similarly, the use of hexa (urea) chromium chloride firstly published in 1929 and claimed by Geigy AG (BP7U1, 638, 775, 005) is a tedious method to be applied industrially, and hence the expert recommended elimination of that technique.

The research group has been acquainted with different diazotisation procedures, especially diazotisation with nitrosyl sulphuric acid. The procedures have been demonstrated in the laboratory during the expert's visit.

2. The following problems have been discussed at the Hamhung chemical complex:

----The poor quality of disperse black 1 is attributed to the grinding techniques. It was recommended to use a Sand Mill in order to obtain sub-micron dispersions having good application properties.

----It was claimed that the yield of malachite green is always low. This is due to the lack of quality control techniques. The activity of lead dioxide must be precisely determined because more or less of the quantity required will affect the yield badly. It was also advised to equip the basket centrifuge with a hot air pipe to dry the product during filtration. Thus, the following drying process could be avoided and transportation losses would be minimized.

3. The dyeing techniques followed in the textile mills for dyeing vinalon are modern and precise, but applicable only for dyeing loose fibres, tensionless rope form dyeing. Problems were observed when dyeing polyester/wool blends with disperse dyes due to staining on wool. It was advised to

try several disperse dyes first in the laboratory to examine their tendency to stain on wool and then recommend use of the dispersol dyes which have low staining tendency.

B. Exchange of knowledge, technical information and training of staff

1. Two lectures were presented at Institute of Organic Chemistry, Academy of Science Branch, Hamhung, covering the following topics.

- Introduction to dyestuff research
- Management of dyestuff research in connection with available raw materials, production facilities, and end user requirements
- Metallization of azo dyestuffs
- Neutral chromium complex dyes especially the 1:2 chromium complex
- Methods of preparation of chromium complex dyes
- Categorizing coupling components to obtain the full range of colours.

2. One seminar was held at the dyestuff research laboratory, Institute of Organic Chemistry, covering the following subjects:

- Difference between organic synthesis and dyestuff synthesis
- Methods of evaluation of the dyestuffs prepared in the laboratory
- Techniques of finishing and standardization of dyestuffs
- Strengthening the notion that dyestuff research should be technology oriented, aiming at manufacture of valuable commercial products. As an example, the research group thought that it must try to prepare the meridial isomers of the metal complex dyestuffs which reportedly have superior dyeing properties compared with the facial isomers. The expert clarified that this is theoretically possible but it is a tedious process to separate the isomers with successive chromatographic separations and X-ray diffraction identification. The outcome of the research would lead to the conclusion that the preferred isomer is highly expensive and that the results achieved have no commercial value.

3. Illustration of the technical procedures for evaluation of laboratory-prepared dyestuffs.

- A copy of the standard methods for fastness tests was delivered to the chief of the dyestuff research laboratories.

----A copy of brochures on laboratory dyeing machines was presented.
The expert recommended the necessary technical requirements.

----The importance of thin layer chromatography, spectrophotometric analysis and substantivity dyeing tests was explained. Laboratory experiments were carried out.

4. Training of technical staff on the commercially feasible preparation of 1:2 chromium complex dyestuffs

----A previously prepared orange dyestuff was revised and a new product was prepared by using chromium salicylate complex.

----Laboratory trials for preparation of deep colour dyestuff of the monoazo and disazo types were conducted under the supervision of the expert.

11. OUTPUT

1. The research group of the dyestuffs research laboratory, Institute of Organic Chemistry are misguided by their concept that dyestuff research must be solely process-technology oriented. They have been advised to change their approach and direct the research work towards development of useful industrial production technologies.
2. The research group has been acquainted with the commercially feasible preparation of chromium complex of 1:2 type.
3. A bluish black dyestuff was prepared in the laboratory which can dye vinalon fibre.
4. The laboratory instruments delivered by UNIDO are operated by highly skilled personnel.

III. CONCLUSIONS

1. The research group, guided by its chief who is highly experienced in organic synthesis, has a wide knowledge and intensive literature background and is capable of conducting successful research.
2. The ambitions and talents of the group, as observed, warrant the possibility of preparing all colours of the 1:2 chromium complex dyestuffs.
3. Training of technical staff on evaluation and quality control of dyestuffs, together with furnishing the laboratories with the necessary dyeing equipment, would considerably reduce the number of trials, efforts, and time required.
4. The existing facilities and hitherto gained experience in the operation of the dyestuff production units, are not suitable for the commercial production of vinalon dyestuffs.
5. Production units are lacking modern finishing and quality control techniques to produce high quality dyestuffs.

IV. ACKNOWLEDGEMENTS

The expert would like to express his appreciation of the efficient assistance he received from the representatives of the UNDP office, Pyong Yang. In particular, the expert is grateful to Ms. Sabina Wenzel, who made all the necessary official arrangements.

He also wishes to extend his gratitude to the representatives of the Academy of Science for their kind care and for their efforts to arrange field visits to the industrial centres concerned.

ANNEX I

Field Visits

A. The Institute of Organic Chemistry (IOC), Academy of Science (AOS)
Branch, Hamhung

Attendants:

Kim Jung Bae	Deputy Chairman AOS, Head IOC
Li Seng Dok	Chief Dyestuffs Laboratories
Kim Chang Hoa	Inspector of Foreign Affairs
Kim hyon Ki	
Li hang il	Government counterparts
Hassan Said Mahmoud	UNIDO Consultant

The discussions illustrated that vinalon is the most important textile raw material produced in the country from local resources (coal and limestone). The country imports all its requirements of the neutral 1:2 chromium complex dyestuffs which are considered the main dyes for dyeing vinalon.

The government expected to receive from UNIDO technical assistance in the preparation of these dyestuffs locally.

The suggested steps were exchange of knowledge, technical advice, revision of the presently applied technology, and help in laboratory trials for the preparation of dyestuffs.

B. Hamhung Chemical Complex

Mr. Chon Hi Rjong Chief of Foreign Affairs Bureau

1. Visit to the spinning department of vinalon and production of staple fibres for textile use and continuous filament for non-textile use.

2. Dyestuff production units of the complex are considered as the main chemical dyestuff production units in the country. They are composed of the following units:

2.1 - Production of disperse black 1, the unit is very old and using simple equipment. Coupling is carried out in a wooden vat, filtration in small Nutsche filter without appropriate means of

- washing thoroughly the cake to get rid of electrolytes. Grinding is carried out in an old fashioned micronizer not capable of producing sub-micron dispersions. There are no means of standardization and quality control. Capacity: 10-20 tons/year.
- 2.2 - Sulphur dyes unit, suitable for the production of this cheap type of dyestuffs. However, the small plate and frame filter press does not permit good squeezing of the cake. No effluent treatment was observed. Capacity: 100-200 tons/year.
- 2.3 - Basic dyes unit, used also as pilot plant. The unit is utilized for the production of Auramine G, Rhodamine B, crystal violet, and malachite green. The unit is very small, reactors are 100-150 lt capacity, 50 cm diameter basket centrifuge. No effluent treatment was observed. Capacity: 10 tons/year.

The expert learned that there are two more plants for the production of dyestuffs in the country. They are:

- a. Production unit at Munchon (300 km east of Pyongyang) producing pigment red (para-red) (30 tons/year) and disperse orange (20 tons/year).
- b. Production unit at Nampo (150 km west of Pyongyang) producing benzidine based direct dyes (50 tons/year).

C. Hamhung Wool Textile Mill

The mill performs:

- spinning and weaving of wool fibres from crude wool
- dyeing of vinalon, acrylonitrile, wool, and viscose fibres in the form of loose fibres and cakes.

The dyeing equipment is modern and working efficiently.

Vinalon is mainly dyed in the loose fibre form to avoid uneven dyeings and to make it suitable for blending with other constituents. The visit was accompanied by Mr. Sin Sang hoa, chief of R & D Department.

D. Pyongyang textile mill, one of the biggest textile mills in the country

- Processing of cotton fabrics including: bleaching, mercerizing, dyeing, printing and finishing

----Processing of polyamide, acrylonitrile, and polyester fabrics
including: blended spinning, dyeing, and printing

----Spinning, dyeing, weaving of natural silk fibres

----Dyeing of vinalon in the rope form using tensionless dyeing machines.

The machinery used is modern and working efficiently.