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Vasyl Mezhybrotskyi, Volodymyr Starchevskyy and Lilianna Oliynyk

METHODS OF DITHIODIMORPHOLINE PRODUCTION

Lviv Polytechnic National University
12, Bandery str., 79013 Lviv, Ukraine; vstarch@polynet.lviv.ua

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Abstract. The results of N,N'-dithiodimorpholine (DTDM) production technology refinement including the sulphur monochloride obtaining, product paste washing and its treatment by polyglycols with the aim of dust formation decrease are presented. Using the optimization method the optimum conditions of DTDM production have been determined. The obtained DTDM of high quality has a high yield.

Keywords: N,N'-dithiodimorpholine, sulphur monochloride, technology, adhesion, dust formation.

1. Introduction

N,N'-dithiodimorpholine (DTDM) is used as a curing agent during the production of rubber wares, mainly tires. It favors the thermostable vulcanizates formation, increases the resistance of rubber mixtures to the premature curing and allows to reduce the sulphur content necessary for curing by 5–10 times at the simultaneous introduction of sulphenamide.

In 1977 in Ukraine the DTDM production was placed into operation. The process main studies were: synthesis, expendable washing of suspension, filtration, granulation, drying and packing (Fig. 1) [1].

The product yield was 72–75 % relative to the theoretically possible one. The production was characterized by DTDM low yield and quality, a great volume of sewages, production irregularity (because it depended upon imported raw material – sulphur monochloride) and high dust content connected with DTDM dispersion after drying. Therefore the problem of DTDM production refinement aimed at the increase of the main product yield, decrease of by-products amount and environmental protection is very urgent.

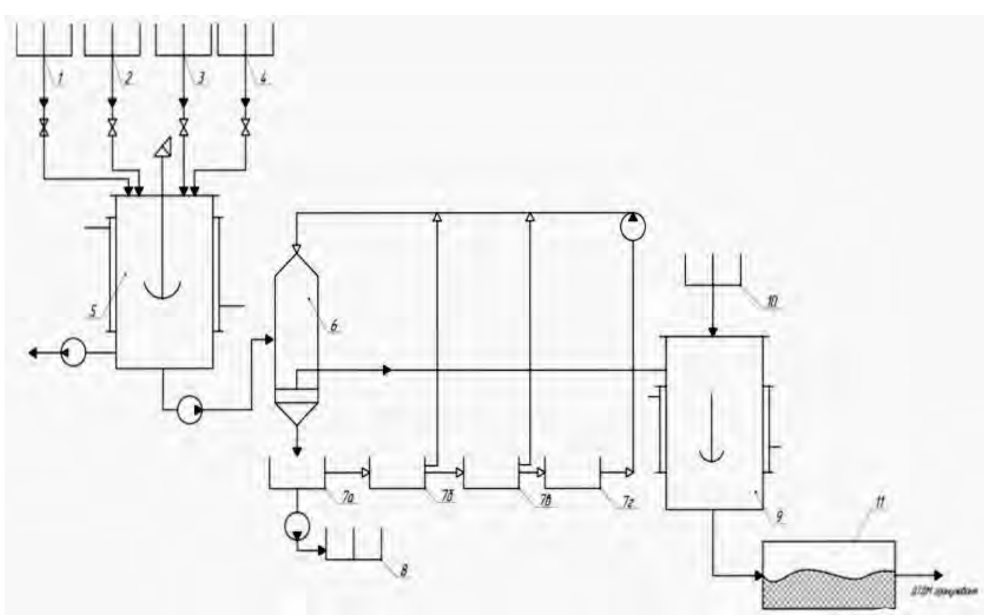

Fig. 1. Process flowsheet of DTDM production existent in Ukraine till 2005: vessels for NaOH, S_2Cl_2, nefras (petroleum solvent) and morpholine (1-4, respectively); reactor with jacket and mixer (5); press-filter (6); vessel for cleansing water (7); receptacle for cleansing water (8); granulator (9); vessel for polyacrylamide (10) and drier (11)

2. Experimental

DTDM purity and quality were controlled using a melting temperature. It should be within the range of 395.0–395.5 K. The quality of sulphur monochloride was controlled by the content of active chlorine within the range of 51–53 %. IR-spectra were recorded using SPECORD M-80 spectrophotometer within the range of 4000–400 cm^{-1}; pellets with KBr were used. To determine the optimum conditions of DTDM production the Box-Wilson method was used.

3. Results and Discussion

3.1. Sulphur Monochloride Obtaining

Sulphur monochloride is one of the components for DTDM production. It is obtained as a by-product at methane chlorination to tetra-chlorine carbon and it was not produced in Ukraine [2]. The problems with import result in the increase of main product cost and do not favor the production regularity. Therefore we studied sulphur monochloride synthesis with the aim of its further production at Ukrainian enterprises. For this aim we used a well-known method of sulphur chlorination in the sulphur monochloride solution, the same as ethylene chlorination to dichlorethane. Though the reaction of sulphur chlorination is described in the literature [3], there are no data for the industrial implementation of the mentioned process.

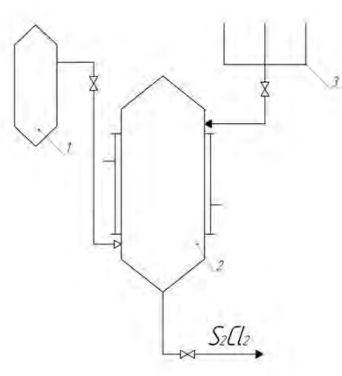

Fig. 2. Process flowsheet of sulphur chrolination: cylinder with Cl_2 (1); chlorinator (2) and vessel with S_2Cl_2 (3)

It was determined by us that sulphur is dissolved in sulphur monochloride at high temperatures. So, we prepared sulphur suspension in the solvent with the ratio of 1.7:1, heated the mixture to 313–318 K under stirring till sulphur completely dissolved and then added sulphur till the ratio became 2:1. Chlorine was bubbled through the solution which was previously blown out by nitrogen. The temperature was 328–333 K; vessel with internal and external cooling was used. After the end of the chlorination process the reaction mixture was sustained for 5 h. Under the mentioned conditions the yield of sulphur monochloride is 98 % with the active chlorine content of 51–53 %, which meets the technical requirements for sulphur monochloride. Thus, in 2005 the stage of sulphur chlorination was implemented in Ukraine. This stage allowed to exclude the raw material import for DTDM production (Fig. 2).

3.2. DTDM Production Technology Refinement

In Ukraine DTDM was produced *via* morpholine interaction with sulphur monochloride in the presence of caustic sodium in the medium of inert organic solvent immiscible with water. The obtained DTDM was contaminated and its yield did not exceed 75 %. The additional final purification resulted in the unproductive losses. The mentioned reaction is very sensitive to different additives affecting the yield and quality of the main product, as well as to the content of dissolved oxygen in the reagents. To eliminate the effect of dissolved oxygen on the DTDM synthesis the process was carried out in the presence of dry sodium sulphite in the system which was previously blown out by nitrogen with 99–99.99 % purity.

We examined the DTDM synthesis depending on the ratio morpholine: sulphur monochloride. The results are described in [4]. Stoichiometric introduction of the initial compounds allows to obtain DTDM of high quality with the yield of 75 %. The increase of morpholine: sulphur monochloride ratio from 2.025 to 2.20 increases the DTDM yield (to 92 %), as well as the melting point. The further increase of morpholine content in the initial mixture results in its unproductive consumption, that is negative for its content in sewages and price of the final product. The increase of process time from 1 to 2 h also does not improve the process performance.

Thus, the main factors affecting the DTDM yield and quality are the excess of morpholine (till 0.1 mol) and absence of dissolved oxygen; that is achieved by the reaction mass blowing by nitrogen with the simultaneous introduction of sodium sulphite. Under the mentioned conditions the DTDM yield is 92.5 %, its melting point is 397–398.5 K [4].

We determined the optimum conditions for DTDM production. The following factors were chosen as those affecting the yield of N,N'-dithiodimorpholine: sodium hydroxide concentration, solvent amount, degree of sulphur(I) chloride dilution, reaction temperature, molar ratio morpholine:sulphur(I) chloride, amount of oxygen acceptor. The results are represented in [5].

Thus, we found the conditions ensuring the DTDM yield of 93–93.5 % and melting point of 397–398.5 K.

The next step was to determine the reasons of DTDM low quality. We analyzed IR-spectra of raw DTDM and DTDM purified by fivefold washing (three times by repulping, then by water with small amount of acetic acid (0.025 %) and then by water). The main compounds worsening the DTDM quality are morpholine and morpholine sulphide. These products, in contrast to DTDM, are well-soluble in water; therefore the washing of paste by water improves the main product quality. It should be noted that in accordance with the existing regulations the DTDM paste is washed by water which is directed to the morpholine extraction with further return for the synthesis stage. Thus the great volume of sewages is formed. We suggested to realize the first and second rinses of the paste by water obtained from the third and fourth rinses (so called repulping). The suggestion allows to decrease almost twice the amount of water without the decrease of product quality. The results are represented in Table.

The existing technology for the tires production provides DTDM usage in the form of granules. Sometimes powder-form is needed. DTDM is a high-dispersive powder, therefore the loss at the drying stage and dust content are great that increases the costs for environmental protection. We examined the effect of adhesive additives increasing the surface attractive forces between DTDM particles. Polyethyleneglycols with the molecular mass of 200, 400 and 1500, as well as B-400 propynol (oxypropylated butyl alcohol) and neonols (surface-active compounds based on C_9-C_{10}) were used as additives. They decrease DTDM dust formation by 10–20 times, and it is sufficient from the ecological point of view. Hence we chose PEG-200 as the cheapest product produced in Ukraine. PEG-200 was dispersed as 50 % solution in water in the vacuum dryer (20 kg of PEG-200 for 1 ton of DTDM).

Thus, the conducted researches allowed us to change the flowsheet of DTDM production (Fig. 3).

Table

Material balance for 1000 kg of N,N'-dithiodimorpholine

Filtration of the reaction mass and washing of N,N'-dithiodimorpholine paste

Receipts			Expenditure		
Products and components	Components mass part, %	Mass flow, kg/t	Products and components	Components mass part, %	Mass flow, kg/t
1. Finished product suspension		9893.4	1. Washed product suspension		5838.8
a) dithiodimorpholine	10.43	1031.7	a) dithiodimorpholine	17.44	1018.3
b) nefras	47.15	4664.0	b) nefras	0.06	3.5
c) sodium chloride	5.36	530	c) water	82.00	4787.8
d) morpholine	1.08	107	d) impurities	0.5	29.4
e) water	32.64	3229.5	2. Manifold, I and II cleansing water		11815
f) impurities	3.34	331.2	a) nefras	38.80	4589
2. First washing by repulping	100	1680	b) morpholine	0.88	103.4
3. Second washing by repulping	100	1680	c) sodium chloride	4.4	525.2
4. Third washing by repulping	100	4000	d) water	53.11	6274.6
5. Water for 4th washing		4001.2	e) dithiodimorpholine	0.14	16.5
a) water	99.97	4000	f) impurities	2.67	306.3
b) acetic acid	0.03	1.2	3. Cleansing water after 3rd and 4th washing		8044.8
6. Water for 5th washing	100	4500	a) water	99.68	8010.8
			b) sodium chloride	0.06	4.8
			c) morpholine	0.044	3.6
			d) nefras	0.19	15.5
			e) impurities	0.026	10.1
			4. Nefras losses		56.0
TOTAL		25754.6	TOTAL		25754.6

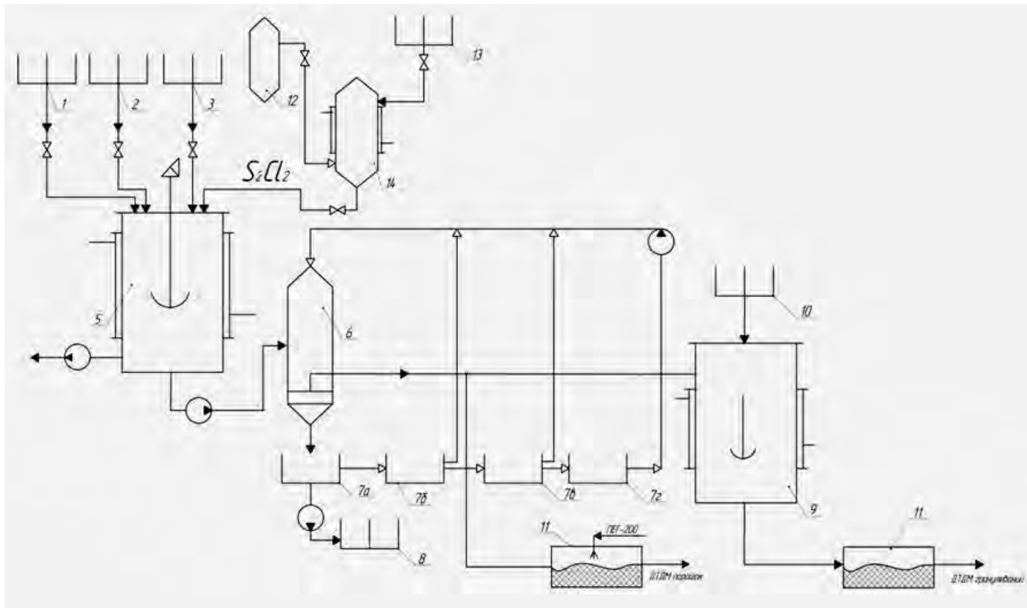

Fig. 3. Process flowsheet of DTDM improved production: vessels for NaOH, S_2Cl_2, nefras and morpholine (1-4, respectively); reactor with jacket and mixer (5); press-filter (6); vessel for cleansing water (7); receptacle for cleansing water (8); granulator (9); vessel for polyacrylamide (10); drier (11); cylinder with Cl_2 (12); vessel with S_2Cl_2 (13) and clorinator (14)

3. Conclusions

Thus, we realized the changes in the process flowsheet: implementation of sulphur monochloride production; change of process conditions with the increase of morpholine: sulphur monochloride ratio; change of washing conditions including repulping and water; drying by dispersed PEG-200 aqueous solution. All these changes increase the DTDM yield from 75 to 93 %, improve its quality, decrease the product cost, almost twice reduce the sewages, extend the DTDM assortment (powdered one without dust formation) and improve the ecological situation.

References

[1] Throdahl C.: Ind. Eng. Chem., 1951, **43**, 421.
[2] Tikavyi V.: Praktikum po Neorganicheskoi Khimii. Khimiya, Moskwa 1969.
[3] Holleman A. and Wiberg E.: Inorganic Chemistry. Academic Press, San-Diego 2001.
[4] Mezhybrotskyi V. and Starchevskyi V.: Visnyk Nats. Univ. Lviv. Poltechn., 2008, **609,** 68.
[5] Mezhybrotskyi V., Chaikivskyi O. and Starchevskyi V: Voprosy Khimii i Khim. Techn., 2012, in press.

ТЕХНОЛОГІЯ ВИРОБНИЦТВА ДИТІОДИМОРФОЛІНУ

Анотація*. Наведено результати удосконалення технології виробництва N, N'- дитіодиморфоліну (ДТДМ), що включає стадії отримання монохлористої сірки, промивання пасти готового продукту та оброблення його полігліколями з метою зменшення пилоутворення. Методом оптимізації знайдено оптимальні умови одержання ДТДМ, що дало можливість збільшити його вихід за високої якості продукту.*

Ключові слова: *N, N'- дитіодиморфолін, монохлориста сірка, технологія, адгезія, пилоутворення.*