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## ON THE PHYSICOCHEMICAL TREATMENT OF WASTEWATER FROM THE MANUFACTURE OF AN ANTIOXIDANT

The antioxidant is a 1,2-dihydro, 2,2,4-trimethylquinoline polymer which displays highly antioxidizing properties. It is widely applied in rubber industry to withstand the influence of atmospheric air, but it may also be used as the basic component of pesticides, insecticides, bactericides, and fungicides.

As the substance of interest has been manufactured so far in a semisolid consistence, it has been diluted with mineral oil prior to delivery to the user. Recently, a novel method has been developed. This yields a solid substance which facilitates transport and meets the requirements of industrial uses. Solidification is achieved by vacuum steam distillation which produces concentrated organic wastewater.

The treatment process involves physicochemical methods: chlorine water oxidation, coagulation and sorption on activated carbon or smoke box dust. Chlorination and sorption on activated carbon give good removal efficiencies. For this method of treatment a continuous process in an ejector system has been developed.

### 1. INTRODUCTION

The parent substance in preparation of the antioxidant is an aniline and acetone condensation product subjected to deactivation and distillation. As the substance thus obtained displayed a semisolid consistence, it had been diluted so far with mineral oil before it was delivered to the rubber-manufacturing plant to be used as an antioxidant. Now, a modified approach yields a solid substance exhibiting a softening point of about 343 K. Two methods are applied to achieve this: 1) distillation, using a thin film-type and a high-vacuum evaporator, and 2) vacuum steam distillation. The method itemized as 2) proved to be more advantageous by involving lower cost and simpler apparatus, and yielding a better end product. Industrial-scale systems make use of this method.

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The manufacture of the antioxidant accounts for the origin of two types of wastewater: those from the production process and those from the concentration procedure, i.e., from vacuum distillation. Their compositions are given in tab. 1. The wastewater displays an alkaline pH, as well as increased coloured matter and organic substance concentrations indicated by the high levels of permanganate COD, dichromate COD and BOD<sub>5</sub>. Total suspended solid concentrations in both types of wastewater samples differ substantially, amounting to approximately 17,000 g/m<sup>3</sup> and 63–73 g/m<sup>3</sup> for antioxidant production wastewater and concentration wastewater, respectively.

Table 1

Physicochemical composition of experimental wastewater

Pollutant	Unit	Wastewater from manufacture of Polnoks R	Concentration wastewater (from vacuum distillation)
pH	pH	11.5	7.6–8.3
Turbidity	g/m <sup>3</sup>	20	20–30
Colour	g Pt/m <sup>3</sup>	320	170
Total alkalinity	g CaCO <sub>3</sub> /m <sup>3</sup>	1075	850–1300
Alkalinity p	g CaCO <sub>3</sub> /m <sup>3</sup>	500	0
Permanganate COD	g O <sub>2</sub> /m <sup>3</sup>	2500	4800–9200
Dichromate COD	g O <sub>2</sub> /m <sup>3</sup>	49000	6560–12500
BOD <sub>5</sub>	g O <sub>2</sub> /m <sup>3</sup>	1600	750–3800
Chlorides	g Cl/m <sup>3</sup>	1320	1.0–2.0
Sulphates	g SO <sub>4</sub> /m <sup>3</sup>	473	13.7
Suspended solids	g/m <sup>3</sup>	16986	63–72
Mineral suspended solids	g/m <sup>3</sup>	8880	12–14
Ammonia nitrogen	g N/m <sup>3</sup>	1.0	1.5–1.8
Organic nitrogen	g N/m <sup>3</sup>	—	8.0

The objective of the study was to investigate the treatment of wastewater generated during concentration of the antioxidant. The treatment process involved physicochemical methods: chlorine water oxidation, coagulation, and sorption on activated carbon or on smoke box dust. The organic components of the wastewater suggested application of biological treatment.

## 2. EXPERIMENTAL

The chlorination process involved chlorine water doses ranging from 140 to 700 g Cl<sub>2</sub>/m<sup>3</sup> and was conducted for 30 minutes. Alum coagulation of the wastewater under study involved alum (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O) doses ranging between 2000 and

10,000 g/m<sup>3</sup>. Adsorption on activated carbon was carried out for 30 minutes with carbon doses varying from 10 to 100 g/dm<sup>3</sup>.

As the adsorption process had proved advantageous, attempts were made to apply smoke box dusts. The dust in question is a waste product generated in the antioxidant-manufacturing plant. The smoke box dust samples were first separated into fractions during flotation. The samples were immersed in distilled water to separate the easy settleable (fraction III) and the top fractions. The top fraction was flooded again and left for 24 h. Surface deposit (fraction I) and bottom sediments (fraction II) were removed and dried for determination of organic and mineral matter.

In order to determine the sorbing capacity of each fraction (with the aim to ensure how they compare to the sorbing capacity of activated carbon), 50 cm<sup>3</sup> wastewater samples (from the concentration process) were treated either with activated carbon or smoke box dust (in 3 g portion each). After shaking (for 1 h) and filtering, pH, permanganate COD and dichromate COD were determined.

In a successive experimental series, the adsorption process was conducted under dynamic conditions in a throughflow reactor (figure) [1]–[3], containing a Carbopol

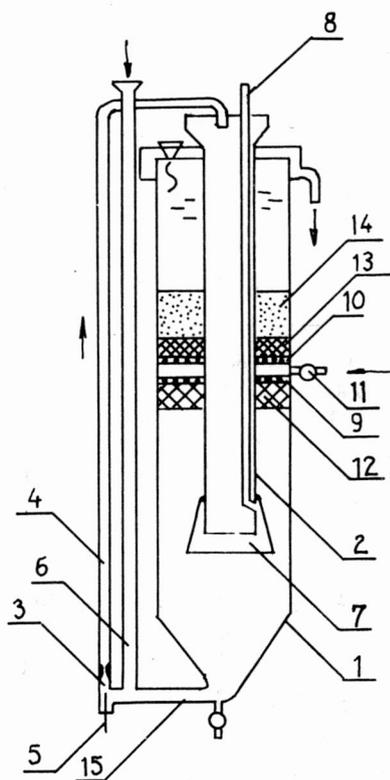


Figure. Multi-purpose ejector system

1 - cylindrical tank, 2 - central pipe, 3 - ejector, 4 - delivery pipe, 5 - compressed air, 6 - pipe for water supply, 7 - gas collector, 8 - vent-pipe, 9-10 - perforated compartments, 11 - pipe for bed wash, 12-13 - elastic polyurethane foams, 14 - sand bed, 15 - pipe connecting the ejector with the cylindrical tank 1

Z-4 activated carbon suspension (20 g), and in another reactor comprising an identical amount of fraction I of smoke box dust.

In this technological system adsorption is considered as a pretreatment procedure followed by the activated sludge process conducted under dynamic conditions in a throughflow reactor [1], [4].

### 3. DISCUSSION OF RESULTS

Wastewaters from the concentration of the antioxidant were treated by physicochemical methods. The experiments were run under static and dynamic conditions for the following unit processes: chlorine water oxidation, alum coagulation, and sorption on activated carbon or on smoke box dust.

The effluent after chlorination and filtration through a filter paper was turbid, yielding permanganate COD removal of 14.1 to 33.7% (tab. 2). Further filtration gave permanganate COD and dichromate COD removal of about 39%, but organics were still persisting in the effluent.

Table 2

Physicochemical composition of wastewater from the concentration of the antioxidant after chlorine water treatment

Chlorine dose g Cl <sub>2</sub> /m <sup>3</sup>	pH	After the first step		After the second step			
		Permanganate COD		Permanganate COD		Dichromate COD	
		g O <sub>2</sub> /m <sup>3</sup>	Removal efficiency %	g O <sub>2</sub> /m <sup>3</sup>	Removal efficiency %	g O <sub>2</sub> /m <sup>3</sup>	Removal efficiency %
0	7.60	9200				12500	
140	6.49	7900	14.1	6200	32.6	8745	30.0
280	6.10	7800	15.2	6000	34.8	8436	32.5
420	5.90	7000	23.9	5900	35.9	8230	34.2
560	5.72	6400	30.4	5700	38.0	8025	35.8
700	5.53	6100	33.7	5600	39.1	7716	38.3

Adsorption on activated carbon was conducted for 30 min and involved doses ranging between 10 and 100 g/dm<sup>3</sup>. The effluent was clear and colourless at a slightly alkaline pH which increased with the increasing carbon dose. Thus, the 100 g/dm<sup>3</sup> dose yielded pH = 9.92 and COD removal of 99.5 to 99.7%. Permanganate COD and dichromate COD measured in the effluent amounted to 28 g O<sub>2</sub>/m<sup>3</sup> and 62 g O<sub>2</sub>/m<sup>3</sup>, respectively. And this means a fairly high degree of removal efficiency (tab. 3).

The effects of alum coagulation (which was conducted with 2000 and 4000 to 10,000 g  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}/\text{m}^3$  doses) are listed in tab. 4. As shown by these data, permanganate COD was reduced by some 25% only. Thus, another sample was treated by chlorination and adsorption (tab. 5). The chlorine water doses applied for this sample were those in tab. 5. After 30 min the sample was treated with a 40 g/dm<sup>3</sup> pulverized activated carbon dose. The effluent was clear and colourless (permanganate COD ranging from 190 to 420 g O<sub>2</sub>/m<sup>3</sup>).

Table 3

pH, permanganate COD and dichromate COD variations in the wastewater from concentration after adsorption on activated carbon

Activated carbon dose g/dm <sup>3</sup>	pH	Permanganate COD		Dichromate COD	
		g O <sub>2</sub> /m <sup>3</sup>	Removal efficiency %	g O <sub>2</sub> /m <sup>3</sup>	Removal efficiency %
10	8.8	5400	41.5	6996	44.4
20	9.07	3150	65.8	3786	69.7
40	9.47	720	92.2	864	95.1
60	—	180	98.0	329	97.4
80	9.90	62	99.5	115	99.1
100	9.92	28	99.7	62	99.5

Another set of samples underwent chlorination (with chlorine doses of 560 to 700 g Cl<sub>2</sub>/m<sup>3</sup>), coagulation (with an alum dose of 2000 g  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ ), pH adjustment (to pH = 7.0), and filtration. The effluent showed a rosy-brownish colour and a permanganate COD removal of about 30% (tab. 6). The effluent after adsorption on activated carbon (a successive step in this combination of unit process) was colourless and showed a significant removal of permanganate COD (over 96%).

As shown by the data in tab. 7, adsorption on smoke box dust under static conditions is less efficient than activated-carbon adsorption. Fraction I displays the best sorbing capacity, yielding permanganate COD and dichromate COD removal of 64% and 73.3%, respectively. The heaviest fraction which settles immediately in water suspension accounts for a 30% removal of both permanganate COD and dichromate COD. The effluent after adsorption on smoke box dust shows permanganate COD and dichromate COD concentrations from 3320 to 6640 g O<sub>2</sub>/m<sup>3</sup> and from 3332 to 8428 g O<sub>2</sub>/m<sup>3</sup>, respectively.

The activated carbon process conducted under dynamic conditions took 6 days to yield a 5 dm<sup>3</sup> volume effluent. The inflow rate, the time of retention in the reactor and hydraulic loading amounted to 0.03 dm<sup>3</sup>/h, 46 h and 0.52 m<sup>3</sup>/m<sup>3</sup> day, respectively. The incoming wastewater had the following parameters: pH, 7.65; perman-

ganate COD, 7400 g O<sub>2</sub>/m<sup>3</sup>, dichromate COD, 11126 g O<sub>2</sub>/m<sup>3</sup>; BOD<sub>5</sub>, 800 g O<sub>2</sub>/m<sup>3</sup>. The effluent permanganate COD, dichromate COD and BOD<sub>5</sub> values were 4200 to 5200 g O<sub>2</sub>/m<sup>3</sup>, 6044 to 6714 g O<sub>2</sub>/m<sup>3</sup>, and 600 to 1000 g O<sub>2</sub>/m<sup>3</sup>, respectively, which gives removal efficiencies of about 30 to 46%, of 42 to 46%, and of 33.3 to 50% for permanganate COD, dichromate COD and BOD<sub>5</sub>, respectively.

Table 4  
Influence of alum coagulation on permanganate COD removal in concentration wastewater

Coagulant dose	Permanganate COD	
g Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · 18 H <sub>2</sub> O	g O <sub>2</sub> /m <sup>3</sup>	Removal efficiency %
2000	8300	9.8
4000	7800	15.2
6000	7400	19.6
8000	6900	25.0
10000	6900	25.0

The adsorption process involving fraction I of smoke box dust was carried out at the following parameters: inflow rate, 0.04 dm<sup>3</sup>/h; retention time, 34.5 h; hydraulic loading, 0.69 m<sup>3</sup>/day. After three days, the treatment effects were considerably higher than those obtained with activated carbon. The effluent exhibited permanganate COD, dichromate COD and BOD<sub>5</sub> concentrations from 2600 to 3700 g O<sub>2</sub>/m<sup>3</sup>, from 3032 to 5039 g O<sub>2</sub>/m<sup>3</sup>, and from 800 to 1200 g O<sub>2</sub>/m<sup>3</sup>, respectively. And this means removal efficiencies from 50 to 64.9% and from 54.7 to 72.7% for permanganate COD and dichromate COD, respectively.

Adsorption on smoke box dust conducted under dynamic conditions had no effect on the removal of BOD<sub>5</sub>.

Table 5  
Permanganate COD variations after chlorination and adsorption

Chlorine dose	Permanganate COD	
g Cl <sub>2</sub> /m <sup>3</sup>	g O <sub>2</sub> /m <sup>3</sup>	Removal efficiency %
140	190	97.9
280	330	96.4
420	420	95.4

Summing up, we can say that the combination of these physicochemical unit processes gave substantial removal efficiencies (90% for permanganate COD and 60% for dichromate COD). Nevertheless, the effluent still showed high concentrations of organic pollutants which made impossible any discharge and called for further treatment. Taking into account the high cost of the chemicals involved (chlorine, alum and activated carbon doses amounted to  $700 \text{ g Cl}_2/\text{m}^3$ ,  $2000 \text{ g}/\text{m}^3$  and  $20 \text{ g}/\text{dm}^3$ , respectively), the applications of these treatment methods in engineering practice was without any promise.

Table 6

Permanganate COD variations after chlorination, alum coagulation and adsorption on activated carbon

Chlorine dose  g $\text{Cl}_2/\text{m}^3$	Permanganate COD			
	After chlorination and coagulation*		After adsorption	
	g $\text{O}_2/\text{m}^3$	Removal efficiency %	g $\text{O}_2/\text{m}^3$	Removal efficiency %
560	6200	32.6	260	97.2
700	6500	29.3	310	96.6

\*  $2000 \text{ g Al}_2(\text{SO}_4)_3 \cdot 18 \text{ H}_2\text{O}$ .

The high removal efficiencies achieved by the sorption process directed our attention to the possible use of smoke box dust as the sorbent medium (the dust in question is a waste material produced by the antioxidant-manufacturing plant). For these needs, adsorption was carried out under dynamic conditions in a multi-purpose reactor with an intensive recirculation of the smoke box dust suspension,

Table 7

Physicochemical composition of the effluent from adsorption ( $60 \text{ g sorbent}/\text{dm}^3$ )

Adsorbent	pH	Permanganate COD		Dichromate COD	
		g $\text{O}_2/\text{m}^3$	Removal efficiency %	g $\text{O}_2/\text{m}^3$	Removal efficiency %
Activated carbon	9.85	240	97.4	784	93.7
Smoke box dust					
fraction I	7.14	3320	63.9	3332	73.3
fraction II	7.81	4880	47.0	5802	53.6
fraction III	9.57	6640	27.8	8428	32.6

which consisted of a very fine fraction. The results were similar to those obtained with activated carbon under identical conditions.

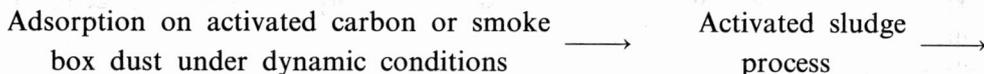
Sorption on activated carbon or smoke box dust was followed by biochemical treatment in a two-stage system: in two reactors connected in series. The degree of organic matter removal was significant, and the effluent permanganate COD and dichromate COD concentrations amounted to at most  $200 \text{ g O}_2/\text{m}^3$  and  $500 \text{ g O}_2/\text{m}^3$ , respectively.

#### 4. CONCLUSIONS

1. The treatment of wastewaters from the concentration of the antioxidant by physicochemical methods (chlorination, alum coagulation and sorption) requires high doses of chemicals, yielding organic matter removal (in terms of COD) between 60 and 90%. The effluent displays high COD levels (up to  $7000 \text{ g O}_2/\text{m}^3$ ), which makes it unfit for discharge either into a watercourse or to the sewer system.

2. Adsorption on smoke box dust gives almost the same results as adsorption on activated carbon, provided that the following conditions are fulfilled: a) the dust fraction is to be separated by flotation after 24 h, and b) the process must be conducted under dynamic conditions involving intensive recirculation of wastewater with a smoke box dust suspension in them.

3. Biological treatment following sorption on activated carbon or smoke box dust yields an effluent which is fit for discharge into the sewer system. To achieve satisfactory removal efficiencies the following block diagram is suggested:



#### REFERENCES

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- [3] GOMÓLKA E., *Rozwój laboratoryjnych urządzeń strumieniowych do napowietrzania osadu czynnego. Nowa Technika w Inżynierii Sanitarnej. Wodociągi i Kanalizacja*, Arkady, Warszawa 1970.
- [4] Polish patent no. 119207.

#### OCZYSZCZANIE ŚCIEKÓW POWSTAŁYCH PODCZAS PRODUKCJI ANTYUTLENIACZA

Antyutleniacz, który jest polimerem 1,2-dwuhydro, 2,2,4-trójmetylocholinoliny, znajduje zastosowanie w ochronie różnych materiałów przed działaniem tlenu atmosferycznego, a także jako składnik pestycydów, insektycydów oraz środków bakteriobójczych i grzybobójczych.

Dotychczas antyutleniacz produkowano w postaci półstałej, następnie rozcieńczano go olejem mineralnym i sprzedawano w stanie ciekłym. Obecnie opracowano metodę zestalania polimeru przez destylację próżniową. W tej postaci antyutleniacz jest łatwiejszy w stosowaniu i transporcie, lecz podczas zestalania polimeru powstają stężone ścieki organiczne.

Aby oczyścić te ścieki, wypróbowano następujące metody fizyczno-chemiczne: utlenianie wodą chlorową, koagulację, sorpcję na węglu aktywnym i pyłach dymnicowych. Najlepsze wyniki daje adsorpcja i dla tej metody opracowano ciągły sposób prowadzenia procesu w urządzeniu strumieniowym.

## ОЧИСТКА СТОКОВ ИЗ ПРОИЗВОДСТВА АНТИОКИСЛИТЕЛЯ

Антиокислитель, являющийся полимером 1,2-двугидро, 2,2,4-трёхметилохинолина, применяется в защите разных материалов под воздействием атмосферного кислорода, а также как составная часть пестицидов, инсектицидов, бактерицидных и грибоцидных средств.

До сих пор антиокислитель производили в полутвердом виде, затем разбавляли его минеральным маслом и продавали в виде жидкости. Сейчас разработан метод отвердевания полимера через вакуумную дистилляцию. Антиокислитель в таком виде легче транспортировать и употреблять, но во время отвердевания полимера возникают концентрированные органические стоки.

Для очистки этих стоков испробованы физико-химические методы, такие как: окисление хлорной водой, коагуляция, сорбция на активном угле и пыли из дымовой камеры. Наилучшие эффекты дает адсорбция и для этого метода разработан способ непрерывного ведения процесса в эжекторном устройстве.