

The Physical-Chemical treatment Of Tanner Effluents 1994

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Like many other industrial processes, the manufacture of leather involves the creation of contaminated effluents, solid by-products or wastes, and the emission of substances in the exhaust air.

Despite intensive action by industry resulting in a substantial reduction of environmental pollution, the introduction of increasingly stringent legislation can be observed in a number of countries in the wake of generally enhanced awareness of environmental Problems. In Germany, according to the Water Resources Policy Act, requirements for the introduction of effluent into waterways are laid down in a waste water administrative regulation. Separate effluent streams containing so-called hazardous materials are subject to requirements based on the State of the art. What this means for effluent originating from the manufacture of leather is that the effluent stream containing sulphide, the effluent from soaking, liming and deliming, including the rinse float and also the effluent stream containing chrome, the effluent from tanning including sammying and neutralization, and from the post-tanning, retannage, dyeing and fatliquoring processes, including the rinse floats, must be pretreated, also in cases where an indirect discharge is used, i.e. before discharge into the public sewage System. The limiting values to be achieved have been defined at 2 mg/l for sulphide and 1 mg/l for chrome (in total) in the respective effluent streams. The principle of separate effluent stream treatment is intended to do justice to the idea that the hazardous substances should be removed from the waste water at as early a juncture as possible in order to avoid dilution by other effluents, i.e. to avoid contamination of greater volumes of effluent and of the sludge resulting from the effluent treatment process. In the event of Joint treatment of the effluent streams containing sulphide and chrome, it is necessary to achieve the same level of contaminant reduction as when using separate treatment processes, i.e. for example with a ratio of 1 to 1 for the two different streams, the resulting limiting value for chrome is 0.5 mg/l.

For tanneries which are not able to operate their own sewage plant complete with biological purification stage, it is therefore ideal for effluent streams containing sulphide and chrome to be collected straightaway in separate Channel Systems. In the training tannery in our institute, where a suitable pilot plant for chemical-physical effluent pretreatment was to be installed, we do not have this possibility. For this reason, floats containing sulphide and chrome may only be run off in sequence into the same Channel. After passing a coarse filter which was installed to avoid pipe blockages, the different types of effluent are fed to separate pumping pits. From here, they are pumped into the respective treatment tanks.

The effluent stream containing sulphide can be treated according to two different principles: either by precipitation using ferrous salts or by oxidation of the sulphide using suitable oxidation agents. As the precipitation process creates a high volume of sludge which must be de-watered before disposal, and as landfill space is now at a premium in our country meaning spiralling disposal costs, we decided in favour of the sulphide oxidation process using atmospheric oxygen.

During previous research work carried out at our institute using a loop reactor (Fig. 1), we were able to ascertain the importance of the presence of manganese(II) salts as a catalyst to the sulphide oxidation process. Without manganese salt, the oxidation process runs extremely slowly, as you see here.

After an initial rapid reduction of the sulphide content from approx. 800 mg/l to around 10-40 mg/l after 1 h (Fig. 2), following a further 6 hour aeration period a subsequent reduction to approx. 5-10 mg/l was observed. In order to be sure of complying with the required sulphide limiting value of 2 mg/l, it may be necessary to add hydrogen peroxide as an additional oxidation agent before releasing the effluent. The use of hydrogen peroxide alone cannot be considered as an Option for reasons of costs, apart from the fact that this oxidation agent also reacts with other substances present in the effluent so that stoichiometric application with regard to the sulphide content is by no means sufficient. According to our experience, with a residual sulphide content of 10 mg/l, it is necessary to add approx. 0.5 l of hydrogen peroxide per m³. As preliminary experiments had shown that oxidation took place more quickly in the less alkaline pH range, we also provided for the possibility of lowering the pH before sulphide oxidation in the pilot plant.

Aeration in the 4.5 m high, 15 m³ capacity tank (Fig. 3) was effected initially by means of jets in the blades of an agitator. At a later time, we intended to investigate the use of a diaphragm plate aeration System. It is possible to meter the hydrogen peroxide used for oxidation of the residual sulphide content in the outlet of the treatment tank.

During experiments in which we varied the catalyst application with 50-200 mg/l of manganese(II), a 24 h aeration period was necessary in each case in order to reach the limiting value of 2 mg of sulphide per litre. The initial sulphide concentrations were around 200-500 mg/l during these experiments. Experiments to determine pH dependency which were carried out using this aeration System indicated that a reduction of the pH to 10 had hardly any influence on the reaction speed. However, problems also arose during these experiments with blocked jets, as the pH setting had been effected using carbon dioxide, and the jets of the agitator tend to become blocked with calcium carbonate. To continue the experiments, therefore, diaphragm plate aerators were installed which were less susceptible to failure. Table I provides a representative collection of results recorded for sulphide oxidation with differing aeration processes.

Figure 1 to 3:

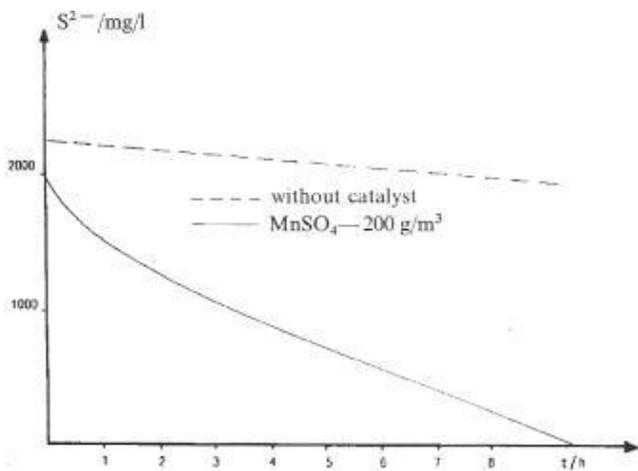


Figure 1. Sulphide oxidation of a Na₂S solution in the 'loop reactor' (air — 20m³/h).

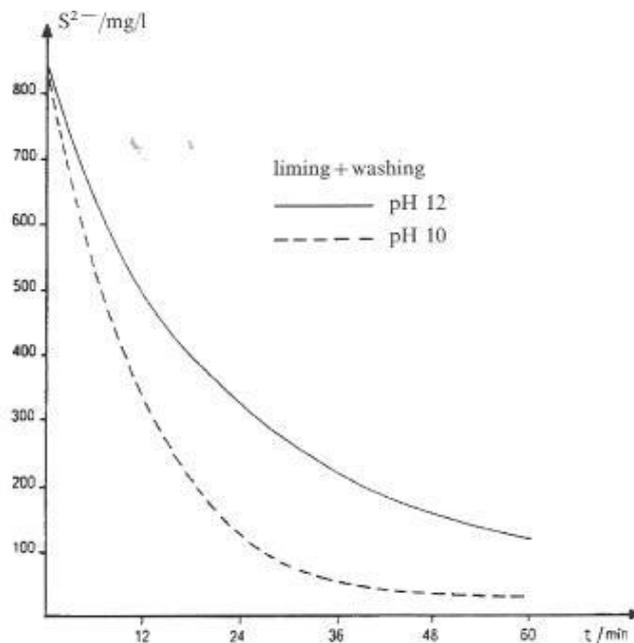


Figure 2. pH-dependence of sulphide oxidation.

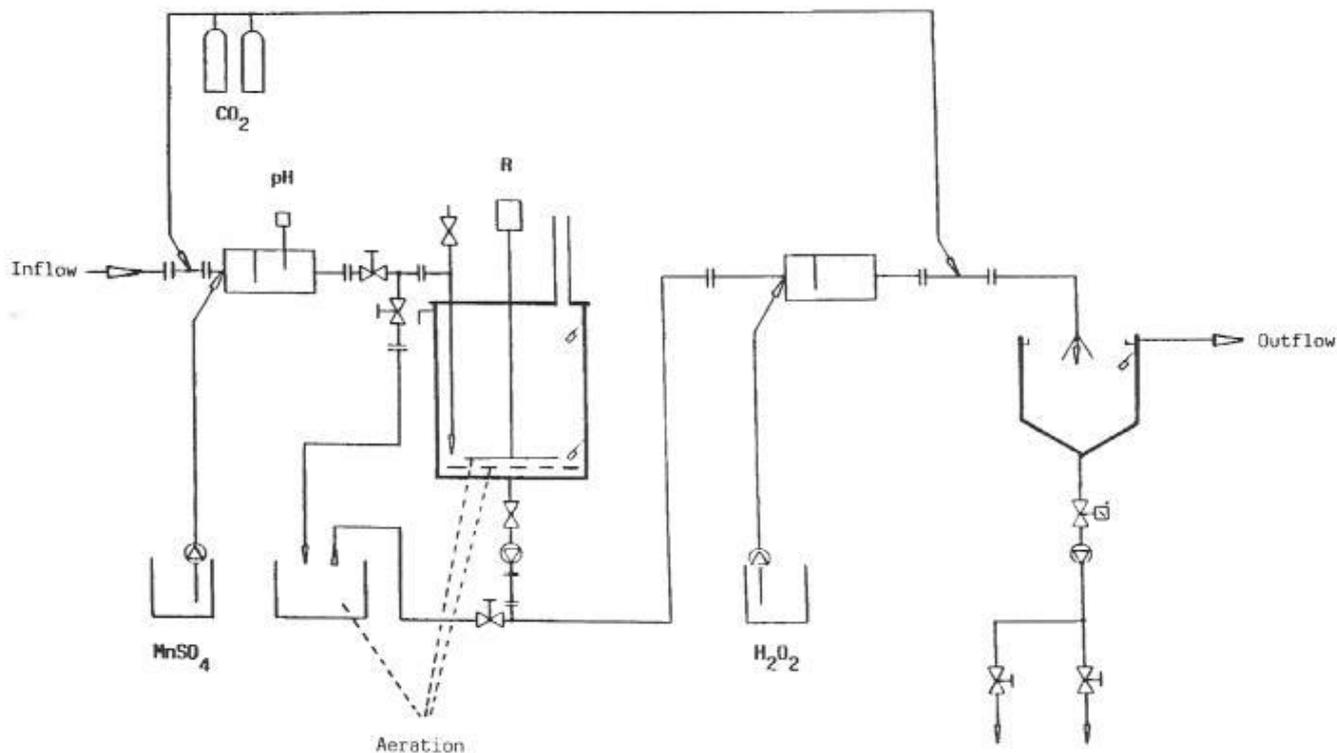


Figure 3. Scheme — Treatment of sulphide-containing effluents.

For the treatment of effluents containing chrome, precipitation of the chrome in the form of hydroxide proved successful in many cases. This process is used with particular success for the chrome recycling of residual tanning floats. However, it is also well known that chrome precipitation in the effluent stream brings about major problems for the wet finishing process. In laboratory experiments, therefore, the precipitability of chrome was investigated in the individual chrome containing residue floats produced during the manufacture of shoe upper leather in our institute (Table II). Precipitation was carried out using magnesium oxide with a pH of approx. Alongside the chrome content before and after precipitation, the COD value of the untreated floats was ascertained in order to recognize any dependency between the precipitation results and COD. Our investigations indicated that it was not possible to reduce the chrome content to a limiting value of 1mg/l using precipitation with

magnesium oxide only. By additional filtration using a fluted filter, we were able to achieve a marked reduction of the chrome content with the exception of residual floats from the fat liquoring and retannage processes. A dependency between chrome precipitability and COD was shown to exist in as far as the floats with increased COD values produced a less favourable precipitation result, which could not be appreciably improved even by supplementary filtration. This points to the fact that, under the influence of fat liquors or syntans, the chrome is clearly held as small particles in a solution or is at least stabilized in the float. These substances contain sulpho groups which can interact with the chrome complexes, for example in the form of ligands. In this case, it should be possible to achieve improvement of chrome hydroxide precipitation by increasing the pH value. On the basis of this assumption, experiment were carried out to test the pH dependency of the precipitation process. The pH value was set using lime milk. At the same time, the influence exerted by the addition of different quantities of an iron chloride additive was investigated, as the addition of ferrous salts had proven successful in practice as an aid to precipitation. Table 3 indicates examples of the precipitation results for effluent resulting from the wet finishing of upholstery leather. The specimens were initially set using lime milk to the specified pH value, and after agitation for 2h the ferrous salt solution and also 10mg/l of polyelectrolyte were added. After a settling period of 2h, the chrome content in the supernatant liquid was ascertained. The results clearly showed that increasing the starting pH value leads to a marked reduction of the residual chrome content in the liquid. In the case of the lower starting pH value 10 and 11, marked improvements can also be achieved by increasing the amount of ferrous salt added, while at pH 12, this has practically no influence.

As the objective of our study was the minimization of the resulting sludge, the influence of the addition of lime milk and ferrous salt on the incidence of sludge was next investigated using a comparable effluent from the wet finishing process on the laboratory scale.

The results of this test, which are indicated in Table 4, indicate that the volume of sludge measured after a settling period of 2h increases markedly with the increase in the addition of lime milk. At the same time, a certain increases of the solid residue also occurs.

Table 1 and 3:

TABLE I
Sulphide oxidation by aeration

Aeration	Air [Nm ³ /h]	Sulfide concentration		
		Start [mg/l]	7 h [mg/l]	24 h [mg/l]
<i>via membranes</i>	12	462	147	3
	22	269	4	2
	44	462	5	3
	44	284	6	2
	44	231	2	
<i>via stirrer</i>	(3 bar)	377	196	2
	(6 bar)	348	21	2

Mn²⁺ – concentration = 50 mg/l in all trials.

TABLE II
Precipitation of Cr in different floats (with magnesium oxide)

	COD [mg/l]	Cr [mg/l]	pH	Sludge vol. (after 24 h) [ml/l]	Cr	
					Filtered [mg/l]	Unfiltered [mg/l]
Cr tanning	2172	2789.0	9.1	70.0	0.9	4.9
Sammying	2898	1221.0	9.1	26.0	3.9	9.9
Washing	225	65.8	9.1	1.0	1.7	12.6
Neutralisation	1932	15.2	9.1	3.0	0.9	2.4
Dyeing	786	7.2	9.1	14.0	0.3	1.2
Dyeing + Fatliquor.	2314	10.5	8.6	0.3	9.4	9.6
Dyeing + Fatliquor. + Retanning	9249	19.8	8.7	85.0	8.3	10.5
Washing	1882	9.1	8.9	13.0	4.3	7.1

Table 3:

TABLE III
Investigations on optimal conditions for Cr precipitation in the effluent of the post-tanning processes

Addition		Supernatant	
Ca(OH) ₂ up to pH	FeCl ₃ [ml/l]	pH	Cr, total [mg/l]
pH 12	1	11.4	1.0
	2	10.6	1.1
	4	9.6	1.2
	8	8.2	1.0
pH 11	1	9.8	10.3
	2	9.4	4.0
	4	8.5	1.4
	8	5.9	n.b.
pH 10	1	9.6	26.4
	2	9.2	11.0
	4	8.2	1.6

The quantity of ferrous salt added was not shown to exercise any influence in the course of this investigation with comparable precipitation results.

Table 4 and Figure 4:

TABLE IV
 Precipitability of Cr dependence on pH and FeCl₃ addition
 Effluent of post-tanning processes
 COD 6440 mg/l pH 3.8 fat 1264 mg/l Cr 58.8 mg/l

	Addition		Supernatant		Sludge	
	Ca(OH) ₂ w=0.05 [ml/l]	FeCl ₃ w=0.13 [ml/l]	pH	Cr, total [mg/l]	volume after 2 h [ml/l]	d.s. [g/l]
pH 12	43.5	2	10.6	1.1	250	2.46
	43.5	8	8.9	1.0	250	2.48
pH 11	35.0	2	9.5	1.8	170	2.46
	34.8	4	9.3	1.0	160	2.32
pH 10	26.8	2	9.3	9.9	90	1.75
	27.4	4	7.9	1.8	110	2.00

w = mass portion.
 d.s. = dry substance.

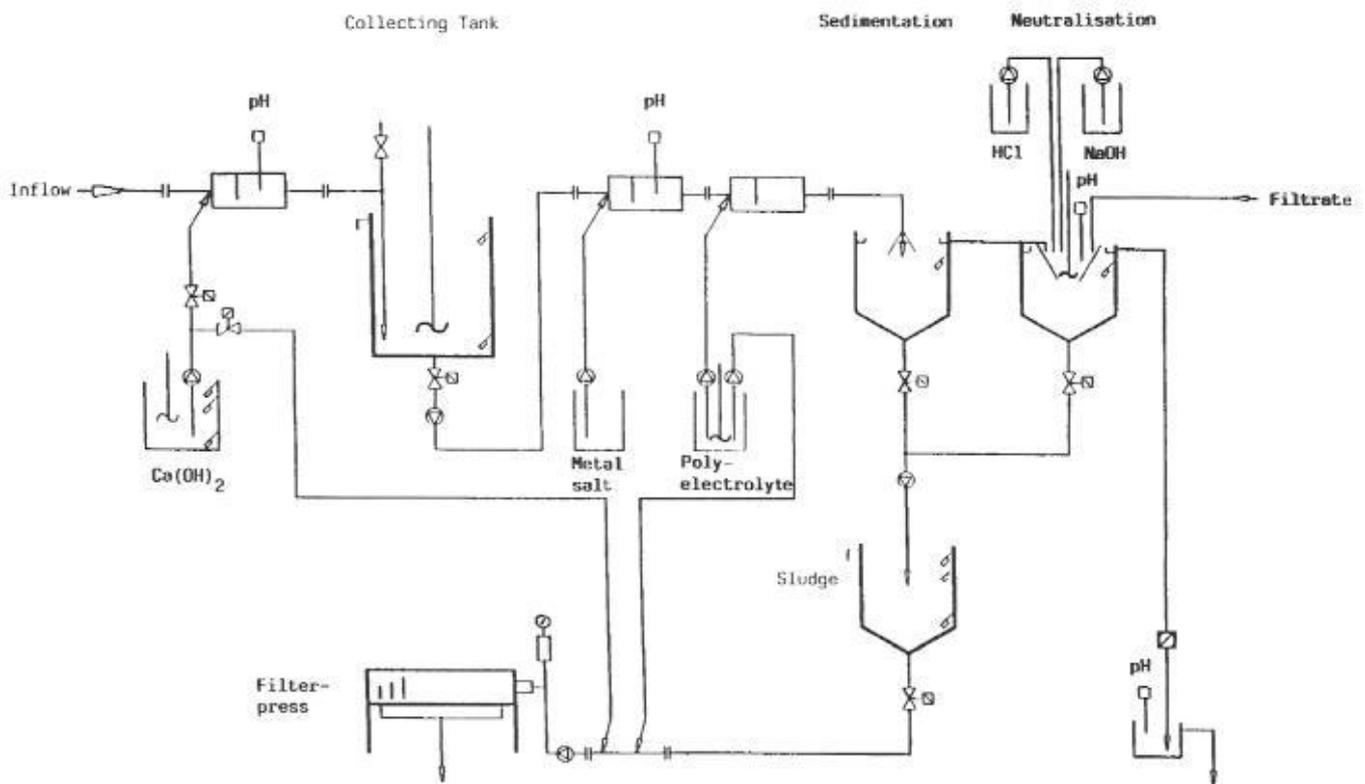


Figure 4. Scheme-Treatment of Cr-containing effluents.

To allow the results obtained during our precipitation tests to be applied in practice, however, the possibility of executing the necessary tests using a pilot plant is extremely useful. In our plant (Fig. 4), the effluent containing chrome is initially fed to a 6 m³ collecting tank, where a pH control System adds the necessary quantity of lime milk. A level control device is used to regulate pumping of the effluent into the settling tank, during which process precipitation agents can be added. The overflow from this tank is transported to the post-neutralization tank where the required pH value can be set for discharge into the public sewage System. The precipitated chrome sludge is transported to a collecting tank from which the compartment type filter press can be fed if required.

During the period of the investigation, the chrome content of the effluent to be treated was between 20 and 210 mg/l. In order to set a pH value of approx. 9.5 in the collecting tank, a value of between 670 and 2730 g of calcium hydroxide were required per m³.

With the various experimental settings in which not only the pH in the collecting tank but also the

ferrous salt additive was varied, we also intended to ascertain the incidence of sludge. It was not possible to obtain an easily pressable sludge in every case, with the result that in these cases in practice an additional filtration aid would have to be used. This, in turn, would lead to an increase of the sludge quantity and so also to an increase in the related costs. In Table V, some sample results from these investigations are summarized. These results clearly indicate the customary process-related fluctuations affecting the properties of the effluent flow from the wet finishing process, and therefore also the chrome precipitation capability. Increasing the pH value in the collecting tank from 9.5 to 12 does not bring about any improvement in the case of this effluent from the manufacture of shoe upper leather. In contrast to the experiments carried out with corresponding floats from the upholstery leather production process. There is a tendency for the precipitation agents, but at the same time the incidence of sludge is markedly increased and the salt content of the effluent is also markedly increased. In one case, for example a 2 ½-fold ferrous salt addition led to a reduction of the pretreated effluent from the production of shoe upper leather, it proved possible to achieve a reduction of the chrome content from 1.7 mg/l to 0.3 mg/l in the permeate. However, we do not as yet have any results relating to the long-term use of diaphragm filters. Initial estimates indicate that with an incidence of 360 cubic metres of effluent per day, a filtration area of around 150m² would be required. This would involve a plant investment of around 750,00 DM simply to permit this supplementary purification process, as experiment to test the use of diaphragm filtration on non-pretreated effluent streams containing chrome have so far not been successful.

In our search for possibilities to minimize the incidence of sludge in the treatment of effluent containing chrome, the use of basic aluminates as a precipitation agent proved promising during laboratory testing. Compared to precipitation using ferrous salts or an acid aluminium salt, the use of an aluminate, whose pH value setting permits operation without the addition of lime milk, results in a reduction of the occurring dry sludge matter by a third. This substantial advantage is retained even in comparison to cases where calcium hydroxide alone is used, which in the case of this unproblematical effluent resulting from the production of shoe upper leather, is sufficient to achieve a chrome content of below 1mg/l. When applying the laboratory findings to the pilot plant with a compartment type filter press, however, it still remains to be seen whether the comparatively bulky sludge permits sufficient compressibility.

As long as the combustion of sludge containing chrome has not been sufficiently investigated, and the relevant facilities are not available, landfill remains the most important method of disposal. Alongside the requirement of a solids content of at least 35%, which can possibly be achieved by adding filtration aids or subsequent sludge drying, the elution process is of particular significance.

However, to date this is not governed by any standardized legal rulings, even within the Federal Republic of Germany. In the Federal State of Baden-Württemberg, one of the main centres of the German leather industry, however according to a recent ruling, the joint deposit of effluent purification sludge from tanneries with household refuse is now generally subject to eluate criteria. This ruling specifies maximum values of 1.5mg/l AOX, 1 mg/l chrome (total) and 0.1 mg/l Chrome(VI) in the eluate which may not be exceeded. According to investigations carried out to date, the filter cake produced in our pilot plant is easily able to comply with the limiting values for AOX and Chrome(VI). The chrome(total) content in the eluate, however, is subject to fluctuations between 0.6 and 2mg/l. Ageing plays a particularly important role here, as the substantially higher values for freshly precipitated sludges indicate. We will be looking at this problem and the question of further-reaching reduction of the incidence of sludge within the framework of our on-going investigations.

Table 5 and Table 6:

TABLE V
 Cr precipitation in the post-tanning effluent of upper-leather production

pH (collect. tank)	Ca(OH) ₂ [mg/l]	pH outflow	FeCl ₃ [mg Fe/l]	Poly-electrolyte [mg/l]	Cr		Filter-Cake [kg/m ³]	d.s. [kg/m ³]
					Inflow [mg/l]	Outflow [mg/l]		
12.1	865	6.4	472	4	52	<0.5	6.7 (28.0% d.s.)	1.9
11.8	850	8.5	208	11	74	1.4	6.7 (22.5% d.s.)	1.5
12.0	4000	11.6	93	15	125	2.1	7.0 (33.4% d.s.)	2.3
9.5	677	7.1	35	10	70	1.7	6.5 (21.0% d.s.)	1.4
9.6	729	7.1	144	12	39	0.7	5.6 (27.0% d.s.)	1.5

d.s.=dry substance.

TABLE VI
 Sludge amount produced in dependence on the precipitants
 Effluent from post-tanning processes of upper-leather
 COD 2470 mg/l Cr 25.7 mg/l

Addition of Precipitants			Supernatant			Sludge	
Ca(OH) ₂ [mg/l]	pH	Product	[mg/l]	pH	Cr, total [mg/l]	Volume [ml/l]	d.s. [g/l]
511	11.0	FeCl ₃	98 (Fe)	8.2	0.4	150	1.5
511	11.0	Al ³⁺	126 (Al)	7.1	0.7	240	1.7
—	—	[AlO ₂] ⁻	76 (Al)	9.1	0.9	220	1.0
511	11.0	—	—	—	0.9	160	1.4

d.s.=dry substance.

H.-P. Germann, G. Renner, The Physical-Chemical Treatment of Tannery Effluents, JSLTC 79, 1994, p. 76-81

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