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Heavy Metal Precipitating Agent for Effluent Treatment

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Heavy Metal Precipitating Agent for Effluent Treatment

Many modern aqueous metal finishing processes incorporate strong complexants, resulting in very stable heavy-metal complexes being present in their effluents. Thanks to the continuing development of ever more efficient rinsing technologies, the concentrations of metals, salts and organic bath components, both in the rinse baths themselves and subsequently in effluents, has likewise increased. Both developments have resulted in improved quality of deposited coatings providing enhanced corrosion protection and with a reduced environmental impact. Thanks to these new chemistries, hazardous chemicals have been largely eliminated and water consumption, reduced.

In spite of this, the use of new chemical compounds, often at significantly higher concentrations in the resulting effluent, has created fresh problems and challenges for those operating effluent treatment plants in the metal finishing industry.

The classical approach to effluent treatment in the metal finishing industry as set out in Hartinger's book published in 1992, had reached a limit. Using pure milk of lime or sodium hydroxide as precipitating agents, for example, after preceding cyanide oxidation and/or hexavalent chromate reduction, it was no longer possible, with few exceptions, to achieve the new and lower legally-required heavy-metal concentration limits. In the event, Hartinger in his extensive "Handbook of Effluent Treatment and Recycling in the Metal-Working Industries" devoted barely half a page to heavy metal precipitation using sulphides or the so-called organosulphides, neither of which are nowadays recommended. The most widely used organosulphide is sodium dimethyldithiocarbamate (DMDTC). Since the widespread introduction in the 1970s of EDTA-containing copper plating baths in the printed circuit industry, DMDTC has been one of the most widely used heavy-metal precipitating agents. It finds further use for the effluent treatment from zinc-nickel electroplating, now widely used following the prohibition of chromium (VI) compounds. The widespread use of DMDTC as an agricultural fungicide has also led to its ready availability.

The ban on use of toxic compounds in electroplating solutions as well as the recognition that significant water savings could be achieved in rinsing processes, throws up the following question. From an environmental standpoint, how much is gained if, as a result, large amounts of toxic chemicals are then required to treat such effluents. ? , The toxicity of sodium sulphide vapours and hydrogen sulphide are often underestimated., The latter, in its toxicity, is comparable with cyanide. Very few effluent treatment plant operators seem to be aware of the importance of monitoring hydrogen sulphide emissions from their plant, which can be a time-consuming operation.

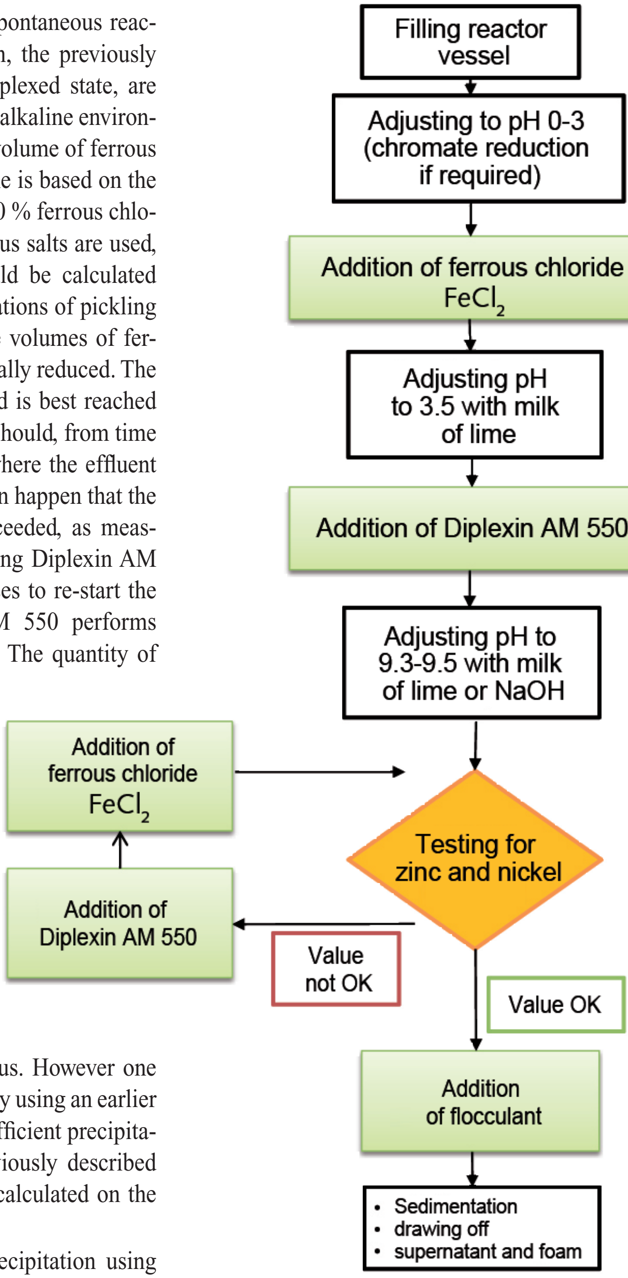
Diplexin AM 550

Further developments and innovations in the field of heavy metal precipitation have as their aim both user-friendliness and the maximum effectiveness. Apart from environmental considerations, the primary aim is to create a product which is either non-toxic or at least with reduced toxicity and one which will reliably precipitate metals, even from strongly bound complexes. Diplexin AM 550 meets these criteria. Thanks to a structure based on cross-linked sulphur-polymers, these molecules are resistant to attack or hydrolysis by weak or even fairly strong acids. In practical terms, this means that Diplexin AM 550 can be used at pH values >2.5 with no danger of hydrogen sulphide being formed. Why is this so important? In the case of sulphides, the optimum metal precipitation pH value lies in the acidic range pH 3 to 6.5, depending on the metal. Apart from this, metal complexes are destabilised at higher H+ ion concentrations, thus making it easier for the heavy-metal precipitating agent to break down the complex.

To provide the best possible solutions for customers, the rate of dosing will depend on the composition of their effluent and/or the particular process being used. When using Diplexin AM 550, an addition of ferrous salts is recommended (typically as the sulphate) in order to bring about de-complexing in strong acid pH ranges. In a second step, at pH 3.5 to 4.5, the metals – now hopefully no longer complexed – are precipitated with Diplexin AM 550 in a spontaneous reaction. In a subsequent neutralisation, the previously added ferrous ions in their uncomplexed state, are precipitated as the hydroxide in this alkaline environment. At least twice the calculated volume of ferrous salts should be added. This guideline is based on the use of the commercially available 20 % ferrous chloride reagent. If other forms of ferrous salts are used, the appropriate dose volume should be calculated accordingly. When higher concentrations of pickling acid are present in the effluent, the volumes of ferrous salts added can be at least partially reduced. The appropriate volume of dosing liquid is best reached by preliminary experiments which should, from time to time, be re-validated. In cases where the effluent composition is highly variable, it can happen that the limiting concentration value is exceeded, as measured at pH 9.5. However, when using Diplexin AM 550, it is not necessary in such cases to re-start the treatment procedure. Diplexin AM 550 performs equally well in alkaline pH media. The quantity of ferrous ions to be added is, as before, in the ratio 1:2 based on the quantity of Diplexin.

In the case of alkaline, chromate-free effluents, it is possible, as would be the case with simple sodium sulphide precipitation, to completely remove heavy metals using Diplexin AM 550 in alkaline solutions. In so doing, economies can be made in the use of acids or alkalis with time savings a further bonus. However one thereby loses the benefits available by using an earlier decomplexing stage with its more efficient precipitation in acid media. As in the previously described cases, dosing with ferrous salts is calculated on the basis of the DiplexinAM 550 used.

The outcome of this combined precipitation using Diplexin AM 550 and ferrous chloride results in a very readily filterable precipitate as a sludge which is easily pressed into cake. This is equally true in the case of more problematic effluents, such as those with a higher concentration of degreasing bath constituents. Where the effluent contains organic compounds, a clear supernatant is seen above the precipitate with the filtrate from the filter press being likewise clear.



Typical process flowsheet for Diplexin AM 550 treatment

A yellow-brownish colouration of the liquor is sometimes observed, typically caused by excessive dosing with sodium sulphide and/or DMDTC. This will not arise when using Diplexin AM 550 while any excess dosing with this reagent will be effectively removed by use of the ferrous salt additions. Thanks to their very different stability constants, there is no danger that ferrous ions will compete with other metal ions or complexes present, in the precipitation process.

Apart from chromium and a handful of exotic metals, ions found in electroplating processes are divalent. In spite of this and notwithstanding very similar precipitation reactions, the various precipitating chemicals used, react quite differently with the metals in question, thanks to their differing affinities. By and large, most sulphide type reagents will precipitate monovalent and divalent metals with no difficulty, while being less successful with higher valent metals. Diplexin AM 550 is specially effective in treating zinc, copper, cobalt and mercury ions as well as, in some cases, strongly bound nickel. Problems in the latter case can be overcome by use of a second heavy metal precipitating agent in combination with the Diplexin AM 550.

Tab. 1: Water Toxicity

	Natriumsulfid	*DMDTC*	*Diplexin AM 550*
EC50 Water flea Daphnia magna	7,1 mg/L	0,67 mg/L	340 mg/L
LC 50 Fish Trout, Bass	25 mg/L	0,76 mg/L	2 080 mg/L

A further feature of Diplexin AM 550 lies in its ability to precipitate metals in their elemental state. In the metal finishing industry, these are rarely encountered, but elemental mercury is often present in waste processing operations or in flue-washings from incineration plants, a notoriously intractable problem where other precipitating agents usually fail.

In addition to the many attractive features of Diplexin AM 550, its very low toxicity should be noted (*Tab. 1*). Thanks to its low eco-toxicity, its German Water Hazard classification is 1 (WGK 1). Its toxicity for the water flea is some 50 times lower than sodium sulphide and 500 times lower than DMDTC.! In terms of fish toxicity, these differences are even more extreme, the toxicities being 80 times lower and 2700 lower than the above-mentioned reagents respectively. These figures highlight the importance of controlling DMDTC concentration by means of ferrous reagents. Especially in the case of smaller effluent treatment plants, there are frequent problems due to over-dosing with DMDTC. This restricts the action of the nitrogen-producing bacteria so that, in many cases, the operator cannot meet the ammonia concentration limit/ Given that effluent dischargers are themselves obliged to hold these limits, it is strongly in their interests not to use DMDTC in such effluent treatment plants. For this reason, the use of DMDTC by individual businesses is forbidden and by judicious use of ferrous salts, its use can be avoided.

Diplexin AM 550 –RedOx controlled

Using Diplexin AM 555, a further development of Diplexin AM 550, an effluent treatment process can be controlled by redox measurement. This allows the dose to be calculated in acidic pH media on the basis of the concentration of metal ions to be precipitated. In consequence, one can thus avoid the conventionally accepted principle of dosing in excess of the calculated value. The process must be one that allows ferrous salt additions – as with alkaline media – after dosing with the precipitating agent. As a result, the very small excess doses over and above the calculated values are removed by reaction with the ferrous salts and the appropriate dosing quantity can be used.

Diplexin MR-1 – Metal-EX Process for Copper and Noble Metals

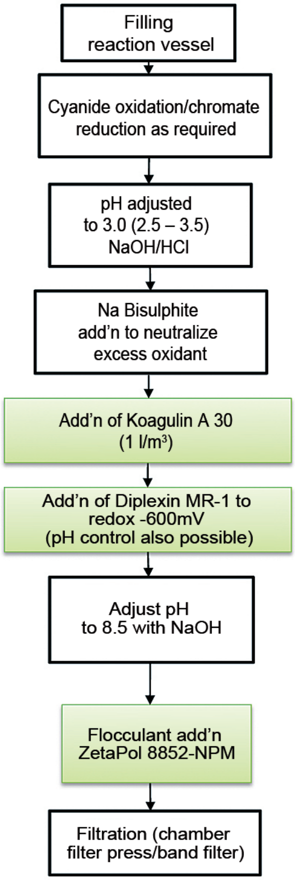
A further development by Messrs Färber and Schmidt, using a physicochemical process, known as "Metal-EX" ensures complete removal of all commonly used more precius metals such as copper, gold, silver, platinum, palladium, rhodium, etc from industrial effluents. These heavy metals are thus completely removed, even when complexed.

Metal-EX does not contain sodium sulphide or organosulphide. Thanks to this, the user has the benefit of a completely eco-friendly treatment compound and is free from any of the concerns noted above, associated with sulphide-type compounds.

The entire process is controlled by means of redox and/or pH measurements and can thus be automated. For the operator, this offers the benefits of the lowest possible starting concentrations of all chemicals involved, optimised reaction times and a minimum use of manpower. Further benefits of the "Metal-EX" process include a large reduction in sludge volumes (40 % to 70 %) as compared with conventional sulphide-iron-based processes. The sludges contain less water and are easily dewatered to yield a clear liquid effluent component. In many cases, batch processing times can be reduced, thereby increasing the throughput capacity of an effluent treatment plant. The illustration shows an electroless copper concentrate after treatment with the Metal-EX process. Note the very small proportion of sludge in the treated effluent as well as the clear supernatant liquor. This process is especially suitable for printed circuit board manufacturers, noble metal platers and those using electroless nickel. However operations involving application of zinc-based corrosion protection coatings will not normally use the Metal-EX process. The process sequence is illustrated in the flow sheet shown.

Electroless copper concentrate after Metal-EX treatment

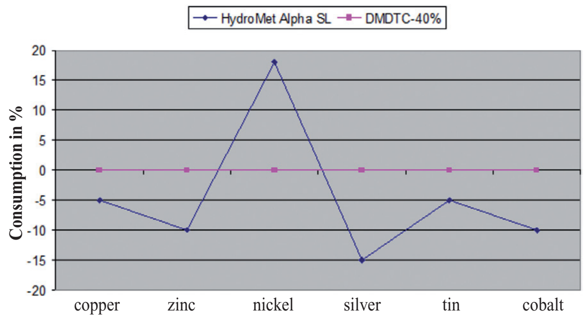
A correctly operating redox process control is an absolute prerequisite for satisfactory operation of such a system. In this case, the process is rapid and largely capable of being automated. Dosing should be triggered by redox values between -580 and -750 mV. A 30 minute reaction time is required. Where no redox process control is installed, Diplexin MR-1



dosing can be carried out on the basis of pH values. Removal of excess oxidant using sodium bisulphite is not possible since the reaction of this compound with Diplexin MR-1 is extremely vigorous and results in massive foam formation. Where there is no alternative, addition of a foam-suppressant can act as a prophylactic.

HydroMet Alpha SL

In the case of the most challenging effluents involving complexed metals, as found with zinc-nickel alloy electrodeposition, it is not possible to reach the prescribed metal ion concentration limits using the classical precipitating agents such as sodium sulphide or DMDTC. Even when excess precipitating agent is used, metal ion concentrations remain too high, or else, after a certain time, begin to increase again. HydroMet Alpha SL (abbreviated HMA-SL) has a basic polymeric structure with a number of functional radicals, consisting of nitrogen or sulphur compounds. Thanks to this complex molecular structure, a range of low-solubility stable metal complex compounds with multiple coordination points can form. Furthermore, these compounds yield precipitates with much improved, flocculation and sedimentation properties in terms of the sludges formed., A well-known problem is that, after adding organic sulphides to effluents containing significant amounts of surfactants, these become extremely turbid, thus causing problems such as reduced treatment rates by the effluent plant. Thanks to the long chain molecular structure of HydroMet Alpha SL and its associated properties, treatment of effluents containing organics is problem-free. An additional coagulation stage with ferrous salt addition and simultaneous removal of strongly turbid supernatant is thereby avoided. After extensive laboratory tests, other research and field trials, this product was first marketed in 2009. Since then, customers in many countries have been quick to appreciate the benefits of this new, eco-friendly and highly efficient heavy metal precipitating agent. Within the HydroMet Alpha product line, there are several variants, including SL, ME/X4, ME/X5 as well as HydroMet Alpha 100, all designed for the processing of effluents containing highlycomplexed metals.



Effizienz Metallfällung

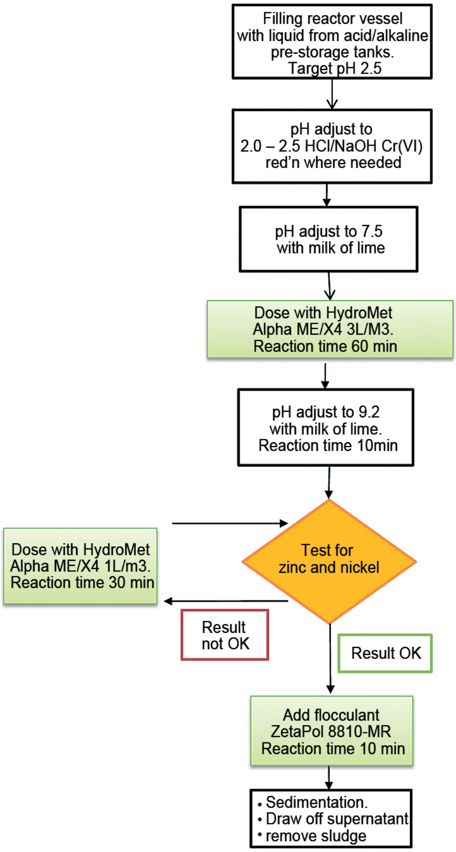
Tab. 2: Eco-Toxicity Comparison

Test/Designation	*HydroMet Alpha*	*Natriumdimethyl-Dithiocarbamet (DMDTC)*
Eco-toxicity	**Results**	**Results**
Fish (OECD 203) EC-50/96h, Poecilia reticulata	> 100 mg/ltr.	2,6 mg/ltr. (minimum 40 x filtered)
Water flea (OECD 202) EC-50/48h, Daphina Magna	> 100 mg/ltr.	0,67 mg/ltr. (minimum 150 x filtered)
Single-cell green algae (OECD 201) EC-50/72h, Desmodesmus subspicatus	50 mg/ltr.	0,26 mg/ltr. (minimum 190 x filtered)
Bacterial toxicity (OECD 209) EC-50/3h	2 000 mg/ltr.	3,65 mg/ltr. (minimum 550 x filtered)
Classification as per CLP Regulation		
Acute water hazard	unclassified	H400 highly toxic to water organisms
Chromic water hazard	H412 long-term damage to water-organisms	H410 highly toxic to water organisms with long-term action
	Caution – irritant	Caution – health hazard Caution – Eco-Hazardous
Water Hazard Classification	WGK-1 Low hazard	WGK-2 water hazardous
Transport & Storage	Non-hazardous Not classified	Hazardous Eco-hazardous material, liquid

For a typical effluent containing complexed metal ions, consumption of HydroMet Alpha SL will be 5 to 15% lower than the quantity of DMDTC required. The more strongly bound the metal complex, the greater the difference between these two types of reagent. In the case of nickel or zinc-nickel where DMDTC offers certain advantages over HydroMet Alpha SL, the use of HydroMet Alpha types MD-E/X4 and MD-E/X5 as well as HMA-100 is recommended on the basis of actual experience.

Some results of ecological and toxicological studies are presented in. Table 2. These show clearly the environmental benefits of HydroMet Alpha SL. The data allows a direct comparison with results using sodium dimethyldithio carbamate.. In addition to the significantly better eco-toxicity results which justify the inclusion of HydroMet Alpha SL in WGK category 1, it is likewise more highly ranked in CLP and ADR classifications than the older conventional reagents. Thus HydroMet is not reportable as a hazardous substance, obviating problems in its storage. HydroMet Alpha is extremely versatile, being usable in solutions from mildly acidic to strongly alkaline. Its use presents no adverse effects on downstream ion-exchange columns. In order to achieve the best possible cost-efficiency, the various types of HydroMet can be used in combination with other heavy metal precipitating agents. Thus, for example, the main heavy metal precipitation could be carried out with Diplexin AM 550 or 555, then, after making the effluent alkaline, removing remaining heavy metals with HydroMet. No further treatment with ferrous salts to remove excess is required. The user is rewarded with a totally clear effluent and a compact filter cake.

A further development in the HydroMet product line was released in 2013, this being HydroMet Alpha ME/X4. The new product was developed in collaboration with a well-known electroplating company and was specially designed to treat effluents from zinc-nickel plating lines.



Treatment sequence using HydroMet Alpha ME/X4

Practical Example

Effluent treatment as described above was carried out several times a day with a batch size of 27 m³. Previously, using the classical approach based on sodium sulphide, combined with DMDTC, the legally-required concentration levels were reached only with great difficulty, using substantial excesses of precipitating reagents. For an effluent containing 940 mg/L zinc and 52 mg/L nickel, the above process now modified by adding 3L/m³ of HydroMet Alpha ME/X4, yielded heavy metal values of 1.7 mg/L zinc and 0.1 mg/L nickel. Thanks to a very reliable downstream ion-exchange unit, no further precipitant was required. Zinc and nickel ion concentrations could be even further reliably reduced by a second HydroMet dosing, but this was not used on account of the additional costs involved. Using this approach, nickel concentrations did not creep back upwards, as was the case when only organosulphides were used. A further benefit stemmed from the fact that using HydroMet products, there was no solution turbidity, and thus no need for a final treatment with ferrous salts. Not only did this reduce sludge volumes, but also disposal costs.

HydroMet Alpha 100

HydroMet Alpha 100 has the same basic structure as HydroMet Alpha SL. However, the molecule is now substituted with the greatest possible number of functional radicals. The resulting reagent is extraordinarily efficient but also somewhat more expensive than the standard HydroMet product. It retains the excellent eco-toxicity rating of its predecessor and thus also its classification, WFG. (Water Hazard Class) 1. For effluents with very high metal ion concentrations requiring doses of>10mL/, it yields a clear supernatant effluent. Many users of this product find that it can treat problematic effluents, when all other approaches have failed.

Zetapol

The wide Zetapol range of products includes mineral-based splitting and flocculating agents based on activated bentonites, Fullers Earth, coagulating agents and other components which ensure reliable flocculation from the widest range of effluents. The very high internal surface area of this range of products results in the efficient adsorption of cloudiness and organics in the effluents being treated. In addition to a high shear strength, the resulting floc has improved dewatering properties. Given these properties, such mineralized flocculating agents are a natural choice for treatment of industrial effluents. It is often heard in the industry that these reagents, on account of their high specific surface area, can absorb heavy metal ions. In the case of very low metal ion concentrations, this may be true, but the effect is so small that in practical terms, these reagents on their own will not significantly reduce metal ion concentrations.

ZetaPol MR and Zetapol NPM Series

Where metal precipitating agents are included in powder form products, the removal of metals is achieved not by formation of weak physical bonds, but rather by means of a chemical reaction to form stable compounds. These are water insoluble solids, readily incorporated within the floc structure of the flocculating agent. Using sedimentation and/or filtration, these metal-containing solids are removed from the effluent. In the case of combination products which contain both precipitating and flocculating agents, their action makes sense only to achieve a given metal ion concentration. Examples might include cases where, after metal ion precipitation, concentrations were only slightly above the prescribed limit or in continuously operating processes with low metal ion concentrations. Should, for example, metal ions at a concentration of 20 mg/L need to be completely removed with a ZetaPol type reagent, the requisite dose would include an unnecessary excess of the other components in this product. A better approach would be to precipitate the metal ions using the reagents previously described and only then complete the process using a ZetaPol type of flocculating agent.

Many users treat their effluents with the precipitating agents described previously to achieve the required concentration limits or come close to these and only thereafter use flocculating agents such as the ZetaPol MR or NPM types partly to save time and also to make quite sure of complying with the specified limits.

Similar measures are also used in practice in combination with HydroMet Alpha ME/X4. The treat-

Tab. 3: Efficacy of ZetaPol products with commonly found metals

	nickel	*copper*	*zinc*	*chromium VI*	*chromium (total)*	*cobalt*	*tin*
Zetapol 8800-MR	+++	+	+	0	0	+	+
Zetapol 8810-MR	+++	+	+	0	+	+	+
Zetapol 8852-NPM	+	+++	++	0	+	+	+
Zetapol 8855-NPM	++	++	++	0	+	++	+
Zetapol 8870-V	0	0	0	++	+	0	0

ment process is concluded with a flocculation and metal ion polishing using ZetaPol 8810-MR. This not only achieves a further reduction in metal ion concentration, but also acts to extend the life of the downstream ion exchanger column. These products are normally used to treat solutions in the pH range 7 to 10. The reagent which is in powder form, is often sprinkled into the effluent plant with the effluent pH substantially unchanged as this takes place. A pH correction using hydrochloric acid may be necessary when using products from some competitors whose products contain chalk or similar alkaline compounds to save money, even though this compromises performance. A pre-dilution with water, often carried out when using polyelectrolytes, should not be done when using powdered splitting and/or flocculation products. This would result in self-flocculation and a loss of functionality. In cases where an automated effluent treatment process is to be used, reagents in powder form can be added using reliable and robust, fully-automated powdered dosing equipment from F & S. Typical stirring times are 15 minutes. The floc so formed adsorbs colloidal turbid materials, has excellent shear strength and settles rapidly. The resulting sludge can readily be dewatered. *Table 1* illustrates the operating mechanism of Zetapol products for the most widely used metals. The particular product in this range used, depends on the combination of metals present in the effluent. Given that these are combined products incorporating splitting, adsorption, metal precipitation and flocculation components, the table serves no more than to provide an overview. The selection of the most appropriate Zetapol type product calls for trials at the customer's premises or in the F & S Customer Service laboratories.

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