

A sustainable alternative to CrVI

Manifest of the Alliance of PVD Providers

The Alliance of PVD Providers (the APP) includes IHI Hauzer Techno Coating B.V., Ionbond Netherlands B.V., Kolzer SRL, Oerlikon Balzers Coating Germany GmbH and Vergason Technology, Inc.

The APP is lead and managed by Fipra International Ltd. who also operates as its trustee to warrant to compliance with anti-trust laws.

17 September 18

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Executive summary

Traditional electroplating uses CrVI, an SVHC. PVD is an alternative. PVD providers are frustrated by the delay in the authorisation process and the RAC and SEAC opinion on Gerhardi application that recommends a disproportionate review period of 12 years.

Without a clear signal from the regulator this innovative and sustainable technology will not be taken up by industry and will move off to China. APP therefore requests the Reach Committee to **speed-up the authorisation processes and shorten the review period of the Gerhardi application to maximum 7 years.**

This is a reasonable request because the opinion has been made on inaccurate information (this manifest provides the latest information). PVD is a sustainable alternative to CrVI and over the last two years PVD has evolved to become technically and economically feasible alternative for PoPAA. Moreover, PVD can meet market demand within 7 years and a 7-year review period would be more in line with the quick development of the PVD technology over the last two years. It is also more coherent with all other EU policies.

1. Introduction

Plating on plastic for Automotive Applications (PoPAA) has for a long time only been possible through hexavalent chromium (CrVI) electroplating. CrVI, however, is a Substance of Very High Concern (SVHC) under the REACH regulation n°1907/2006 and is, as of 20 December 2011, subject to an authorisation process (Annex XIV) in order to protect workers' safety and health and to promote innovative alternatives.

Unfortunately, today - almost 7 years later - this process is still ongoing. It is business as usual for the electroplating value chain and nothing has changed. Not for workers and nor for alternative providers and that while CrVI can cause cancer and government-led investigations are ongoing in for example the Netherlands: see [here](#).

The three Applications for Authorisation (AfA's) are still pending: Lanxess, Gerhardi and Hapoc. The Committee for Socio-economic Analysis (SEAC) and the Committee for Risk Assessment (RAC) within ECHA have recommended the European Commission to grant the following authorisations:

- **Lanxess:** 4-year authorisation for functional plating with decorative character¹, whilst maintaining a 7-year authorisation for other applications².
- **Gerhardi:** 12-year authorisation³ although there were 2 minority positions in RAC and SEAC in favour of a shorter review period!⁴.

¹ Opinion of RAC and SEAC (16 September 2016) on an Application for Authorisation for Chromium trioxide use: Functional chrome plating with decorative character. Access [here](#).

² Opinion of RAC and SEAC (16 September 2016) on an Application for Authorisation for Chromium trioxide use: Functional chrome plating. Access [here](#).

³ Opinion of RAC and SEAC (13 March 2017) on an Application for Authorisation for Chromium trioxide, use: Plating on Plastics for Automotive Applications (PoPAA). ECHA/RAC/SEAC: AFA-O-0000006558-63-02/F see for access [here](#).

⁴ Minority Positions on CT Gerhardi AfA. Access [here](#).

- **Hapoc:** RAC and SEAC have not yet issued a recommendation on this application.

PVD providers are heavily affected by this delay in the decision-making process and by ECHA's opinion of a 12-years review period (hereafter the Opinion). PVD is a sustainable substitute for CrVI used in traditional electroplating and without the right regulatory environment the EU market for PVD will never mature in the EU. Instead, it will mature elsewhere, for example in China or the United States.

For more information please find Annex 1: An APP member's plea "An APP plea: Regulate to make OEMs change to alternative technologies".

2. Problem

Relying on the authorisation process (and in line with the objectives of REACH), APP members have invested in alternative technologies like PVD but delays in the decision-making process and the recommendation by RAC and SEAC of a 12-year review period for the Gerhardi application, have made APP customers, like the original equipment manufacturers (OEMs) slow down on approving and applying PVD.

Some concrete examples:

- [...] reports that [...] was initially planning to extend PVD coatings into new cars, thereby substituting [...] and [...] but, in the end, Renault switched back to electroplating even though PVD was an economically comparable solution.
- [...], reports that before the Gerhardi recommendation, the company was actively engaged with at least [...] European OEMs who were considering purchasing its technology and has since received OEM approvals from several European automobile manufactures including [...]. However, since the Gerhardi opinion only [...] European [...] continued active discussions. The other companies cited the Gerhardi opinion as the reason why they were slowing down their efforts to approve and apply alternative technologies.

If not nudged by the regulator, the customers of PVD providers in the automotive industry do not have enough incentives to change to PVD. Indeed, 12 years is an eternity in business and most people working at OEMs, including its corporate leadership, will be long gone in 12 years.

In addition to the above, OEMs believe that electroplaters bear the prime responsibility for the use of CrVI, not them. As CrVI remains locked after it has been electroplated, health and safety risks only concern electroplaters⁵. Risks with regards to CrVI will only reappear in the stage of disposal (waste) and recycling, which is again not to the concern of OEMs - but will nevertheless hinder a circular economy.

In general, and from the perspective of OEMs, continuing to treat car parts with CrVI remains attractive because 1) the supply chain is already in place and has been working for decades 2) the products are known and the workers know how to work with them 3) the OEMs can guarantee security of supply by using two different technologies in parallel (and in competition with each other this can help to keep the price down)

⁵ An example relates to CrVI baths, used in the process of PoPAA, which need to be disposed of by electroplaters and not the OEMs.

and 4) this will never become a priority in an EU industry that worries much more about existential issues like competition from China and technological advancements in Silicon Valley.

The status quo and perspective of more business as usual, also tilts the level playing field: It permits OEMs to focus exclusively on achieving direct, short-term cost savings while workers safety and environmental aspects are not factored into the connotation of costs (like is the case in, for example, the EU's ETS system), allowing the electroplating supply chain to free-ride and capitalise on these workers and our environment. This is not in line with the ideas of an EU single market and in direct contradiction with the REACH Regulation that has merged these points of view so elegantly together in its objectives *to ensure a high level of protection for human health and the environment [...] and the enhancement of competitiveness and innovation.*

Also, China recently adopted regulations to reduce the amount of waste from chromium plating lines by half and is no longer issuing permits for new plating lines that use CrVI. Consequently, Chinese companies are actively exploring green alternatives to CrVI and European companies are meeting that demand. Oerlikon recently sold⁶ an Inubia I equipment to the Chinese company DFWY [..]. Impact Coatings (Sweden) has delivered an INLINECOATER™⁷ to the Chinese company Xin Point. This will affect the whole supply chain in Europe, including plastic injection moulding and mould making.

The shift to China is not in line with the ambitious EU policies on environment, climate and competitiveness and the APP members therefore urge the European Commission not to let this happen and help these companies to defend the EU's competitive advantage in this innovative and sustainable field.

To conclude, the status quo will not change without a clear signal from the EU regulator and time is of the essence now. **Further delay in the decision-making process and a 12-year review period of Gerhardi will lead to a "lose-lose" situation:** it has and will further reduce the incentives to switch to sustainable, innovative alternative. This is not only detrimental to workers and to the environment, but also to the EU's competitiveness, as the demand for green and innovative alternatives has shifted to other markets like China. Once the use of CrVI will no longer be authorised, which will happen eventually in any case, the EU will find itself empty-handed and dependent on Chinese technologies, know-how and personnel.

3. Solution

Quicker decision-making would be in line with the EU's Better Regulation objectives, provide clarity to the market, legal certainty and hence investment certainty. A shorter authorisation period would spur the market development of sustainable alternatives, such as the one developed by the APP members which is ready for commercial uptake and has the potential to fully meet the entire PoPAA market demand within 5 to 7 years.

The APP is very grateful for the opportunity that DG Environment (ENV), DG Internal Market, Industry, Entrepreneurship and SMEs (GROW) and ECHA have offered them to constructively present and discuss their case on 6 September 2018 and requests the REACH Committee to:

⁶ See [press release](#).

⁷ See [announcement](#).

- **Speed-up the decision-making process:** The APP invites the European Commission to decide on the Gerhardi and Lanxess applications by autumn 2018.
- **Shorten the review period to maximum 7 years:** The APP urges the European Commission to reconsider the disproportionate and unnecessary 12-year authorisation for Gerhardi and proposes to reduce the authorisation to maximum 7 years. This would be in line with the 2 minority positions of SEAC (see [here](#)) and is also justified given the rapid technological developments in PVD technology (see below).

4. Argumentation to support solution

This manifest provides new argumentation to support the above requests. “New” means information dated after 22 June 2016 which was the deadline for the third-party submissions on alternatives to Gerhardi AfA for [...], one of the APP members.

This manifest will illustrate (i) how the regulatory process has been suboptimal in delivering the best societal (most sustainable) outcomes (ii) how PVD has become a technical equivalent to CrVI, (iii) why PVD is a sustainable alternative to CrVI, (iv) how PVD has become economically comparable with electroplating and (v) that PVD has become ready to fully serve the entire market demand for PoPAA within 7 years and last but not least (vi) how this fits within the goals of broader EU policies.

4.1 Decisions have been made on the basis of inaccurate information

The Gerhardi AfA and its AoA contain inaccurate information: some information is highly disputable and moreover most of the information on PVD is now out of date (because of the delay in the process). The Opinion is based on this inaccurate information. This manifest is intended to give the latest available information which, given the principles on better regulation, would have to be considered when formulating the final decision.

The Opinion is based on disputable and outdated information contained in the Gerhardi AfA and its AoA.

Some information provided by the OEMs and conclusions based on that information is disputable:

- Comments addressing the economic feasibility of PVD (see Chapter 4.4) are incorrect.
- Comments implying that PVD fails to pass OEM tests⁸ are incorrect. Already pre-22 June 2016 the PVD process had been approved for the automotive industry through an extended range of field tests. This is supported by the views expressed by SEAC experts Simon Cogen (Belgium), Maria Noring (Sweden) and Lars Fock (Denmark) in their Joint Minority Position (see figure 1).
- Comments addressing the need for regulatory certainty are not convincing. The [Minority Position](#) of SEAC expert Jean-Marc Brignon (France) also covers this (see figure 2).

⁸ "PVD-based processes do not fulfil currently the requirements of the German automotive industry regarding the quality, aesthetic value and functionality of the parts...." (comment by VDA).

Figure 1: Joint Minority Position of Simon Cogen, Maria Noring and Lars Fock

Therefore we do not think that the applicant has satisfactorily demonstrated the long term infeasibility, both technical and economical, of this alternative. As such the AoA, and the information therein, cannot be used as an argument for a long review period.

Figure 2: Minority Position Jean-Marc Brignon

Finally, the applicant also justified the long review period on the rationale that a normal review period would mean regulatory uncertainty for his clients and that they would in reaction turn to another supplier. I found this assertion not enough justified, and I note that the applicants' clients already accepted the uncertainty surrounding this authorization process without turning to competitors. The regulatory uncertainty regarding the review report is not obviously higher than that of the first application and I did not find the argument convincing.

The bias against PVD that can be read into the above, was also experienced by some of the APP members when they were invited to the dialogues. There was no room for / nor interest in a profound discussion about the technicalities or prospects of PVD. Although intentions of the dialogue might be good, this has led to much frustrations for these SME's that were not organised in a consortium back then. APP's recommendation for the REACH review would be that ECHA takes a more pro-active, inquisitive approach in this process.

The information is also outdated. On p. 59 and 60 of the Gerhardi AfA it is mentioned that the PVD brand [...] had been tested but was not regarded as suitable. At the time, [...] was in trial-run. Today, there is a large number of tests where [...] is approved by OEMs. The extensive list (updated until 2018) is attached as a separate Excel file. Based upon the test results products for OEMs are in serial production in [...].

Also, the input of [...], one of the APP members, for example dates back from 22 June 2016, which was the deadline for the third-party submission on the Gerhardi AfA. Since that date, however, PVD has quickly developed: lessons have been learned and implemented, patents have been granted and OEM approvals keep coming in (see chapter 4.3).

If there were to be an excuse for the RAC and SEAC Committee for recommending a 12-year review period, it would be that they did not have the most accurate data. The REACH Committee will not have this excuse. This manifest is intended to give the latest available information which, given the principles on better regulation⁹, would have to be considered when formulating the final decision. The APP is therefore thankful to the Commission who has offered to upload this manifest onto the CIRCABC system.

⁹ Activities of the EC should be evidence based: meaning they are based on the best available evidence including scientific advice, or a transparent explanation of why some evidence is not available and why it is still considered appropriate to act (p. 7 of the [Better regulation "Toolbox"](#)).

4.2 Technical feasibility of PVD (quality)

Since the AoA, PVD has evolved to become suitable for all technical appliances regarding PoPAA with levels of quality that are similar to traditional electroplating. This is demonstrated through a response to each of the alleged limitations cited on p. 33 of the Opinion.

The PVD technology is based on two basic processes:

- The first uses two layers of ultraviolet cured coatings (UV lacquers) to get a metallisation effect. The first layer is the primer, or base coat, which serves to equalise irregularities on the surface of the plastic part. On top of the base coat comes the actual PVD layer, which uses inline magnetron sputtering deposition technology in a vacuum chamber for an exceptionally stable coating with high nanostructure density – with no harmful ions left behind. To protect the metallised coating, a final monocuring UV lacquer (top coat) is applied which is extremely durable, stable and fast-drying.
- The second uses a single layer paint base coating and an engineered chromium matrix to provide the appearance and durability of chromium without actually using CrVI.

In the Opinion on p. 33 it is mentioned that *“at the current stage of development, PVD-based systems cannot be seen as a general alternative due to limitations”* which is illustrated by Table 12 that points out the 2016 limitations of PVD vs. electroplating.

In the Opinion on p. 36 it is mentioned that the applicants *‘highlight that the proposed alternatives do not hold any general approval by the OEMs, and this is confirmed in general terms by another comment submitted in the public consultation (from German Automotive Industry Association). With no general approval for PVD-based processes by the OEMs, any PVD process would need to gain such an approval before it could be considered an available alternative.’*

These statements are incorrect and cannot be a basis for granting a 12 years review period!

PVD passes all required OEM tests .. and de facto is thus already considered by the OEM market to be an alternative to electroplating for PoPAA.

For example: in August 2017 [...] has obtained OEM approval from [...] for [...]. [...] also has received [...] which were assembled on numerous taxis, mainly E-Class vehicles, which were then driven for thousands of kilometers in different climates around the world. The [...] was received in December 2016, and the S2 testing completed in April 2018. [...] has reported positive results and [...] is awaiting a final report, but it has had indications that it has passed all tests. In those test, also other alternative supplier’s coated products have been tested at the same time by [...]. APP has requested this report that lists all results and will provide it, as soon as it has it.

Please note that this is all new information: The test results and approval documents are confidential and in the confidential [...] Annex - available on request.

From 2016 onwards, [...] has received parts approvals from GM (China), VW (Shanghai), Ford, Audi, Daimler and BMW and general approvals from VW, BMW, Daimler and PSA with ongoing qualifications for 2019 for VW Group, BMW, PSA, Fiat Chrysler Automotive, GM-US, Daimler and Jaguar Land Rover

Please note that this is all new information: The test results and approval documents are confidential (please find the confidential [...] Annex - available on request).

In order to give a clear comparison, the APP has mirrored above-mentioned Table 12 to give a 2018 update on the alleged 2016 limitations of PVD versus electroplating. The test results and approval documents are confidential (please find the confidential [...] Annex - available on request).

Table 1: Evolution PVD technology since 2017

Testing	2016	2018	Comments by APP on technical feasibility
Selective coating of 2K/3K components	X	V	Several PVD masking technologies can be used for treating [...] products. It is more precise than electroplating and cheaper as only one single material is required. Masking is more complicated than using materials that will simply prevent the adherence of the coating, but this is an issue that can be solved.
Corrosion resistance	V	V	PVD technology passed corrosion resistance tests ¹⁰ . These tests are approved by OEMs and are up to par with the standards of [...], ASTM (American Society for Testing and Materials) that look at how well the material holds up when treated with copper-acid spray, salt water and Russian mud.
Wear/abrasion resistance	X	V	PVD technology passed mechanical wear resistance tests, which looked at adhesive wear, abrasive wear, wear resistance against chipping (stones hitting the coating). Tests are again in accordance with the standards of the OEM and the ASTM.
Reusability and recyclability	X	V	The lacquer can be recycled and used before drying, but due economic reasons this is not done (but it is possible). The process works as follows: the overspray of lacquer is collected and by a pump collected in a tank. The collected lacquer is dried and disposed as solid material blocks. The used target materials are returned to the supplier and recycled. PVD is a vacuum process and as such there is hardly any leakage except atmospheric gases and minor quantities of process gases that do not need any treatment when pumped away.
Adhesion	X	V	PVD technology passed adhesive tests are within the same category as mechanical wear resistance tests. In adhesive wear tests the adhesion of the coating to the substrate is tested ¹¹ . This is done via so-called 'cross hatch tests', which sticks testing tape on the coating, whilst making deep cuts on the tape through the coating. When the tape is removed, only the sharp cuts should be visible, and no material should be removed with the tape. Another test is the 'saw grind test', checking adhesion after grinding the coated part with a saw.
Weather proof	X	V	PVD technology has passed tests ¹² on the use of coatings in coastal environments, where aggressive sea water leads to highly corrosive environments. Also, the exposure to temperature changes is tested,

¹⁰ The test results and approval documents are confidential (please find the confidential [...] Annex - available on request).

¹¹ The test results and approval documents are confidential (please find the confidential [...] Annex - available on request).

¹² The test results and approval documents are confidential (please find the confidential [...] Annex - available on request).



			especially changes in temperature are causing expansion and contraction of the coating. Lastly, degradation to UV light is tested as well.
Aesthetics	X	V	Beyond the classic chrome color, PVD offers a large variety of color options and structure effects, providing more flexibility in design. PVD can also be used on any kind of plastic. The cold touch can indeed still be better with electroplating, since the plating is much thicker than the PVD coating (less than 0,5 µm vs. 30 µm of metal). However, that is changing rapidly: the blueish colour (as made by CrVI plating) can for example already be made with PVD provided that there are PVD technologies used with high ionization. This is increasing the investment slightly.
Customer acceptance	X	V	There is a large number of tests where [...] is approved by OEMs. The extensive list (updated until 2018) is attached as a separate Excel file. Based upon the test results products for OEMs are in serial production in [...].

.. But there is more: Not only does PVD pass all required OEM tests, PVD offers a set of more innovative features highly attractive to designers, manufacturers and end-users. Among those features, the most relevant are:

- **Translucency:** The thin PVD coatings can be made translucent for light sources beneath the coated part. At night and when dark, coated parts – that look metallic during the day – can provide signal lighting or back lighting, thereby increasing road safety. Also, the inbound and outbound radar transparency of metallized plastic parts is now possible, for example, for safety distance control solutions integrated into the front grills of cars or lane departure warning sensors in the exterior rim.
- **Compatibility other technologies:** PVD does not block GPS, radio and mobile phone waves. This enables the automotive industry to remove antennas, which reduces fuel consumption.
- **Optimized user interface:** Laser etching allows controlled coating removal for day/night design or, for example, for light emitting buttons which can have letters or icons laser-etched into them.
- **Capacity sensing:** The integration of capacity sensing technologies offers attractive design solutions, such as door handles responding to touch or electronic control panels and sliders.
- **Broader choice of materials:** Much wider range of plastic substrate materials, not limited to ABS. this widens the options for cheaper and stronger plastics.

For more information, see Annex 2: APP presentation on PVD technology versus electroplating, shown on 6 September 2018 at the meeting with DG ENV, DG GROW and ECHA.

4.3 PVD is a sustainable alternative to CrVI

Sustainability is like yin and yang. It is as much about protection of human health and the environment as it is about enhancement of competitiveness and innovation. Yin: PVD is a sustainable technology which does not include the use of any SVHCs nor substances considered as having endocrine disrupting properties. Yang:

It is also sustainable as a technology due to its functional characteristics and potential uses, which make it equipped for the digital age.

PVD offers advantages in terms of sustainability: 1) no SVHCs are used in the production process and the process is conducted in a vacuum, thereby eliminating the risks of exposure for workers and leakage into the environment 2) it is estimated that it consumes up to 5 times less energy and hence can reduce the carbon footprint of the treated materials also by a factor of 5 3) PVD treated articles are easier to recycle compared to electroplated parts (as the latter also contain Cu and Ni) 4) PVD does not create hazardous waste at all, while electroplating does.¹³

Not only is PVD more sustainable from an environmental and health point of view, but it is also more sustainable from an innovation and competitiveness perspective.

PVD is used on spectacle frames, for wear protection, on perfume bottles, jewelry (Swarovski uses PVD), sanitary (all producers of faucets use PVD, also for high-end faucets), mobile telephones, watches and more. In all these cases preferred features are appearance and metal-look colours combined with wear protection. Further improvements of PVD beyond today's state-of-the-art may also reasonably be expected as the technology provides advantages beyond mere Cr-metallisation.

Because of their translucency and transmissibility of GPS and other signals PVD lacquers are better fit for the digital age and should therefore become the coating of choice for Europe's (more) autonomous cars, IoT and other fast developing markets in the Industry 4.0. (see for further information Chapter 4.2).

It is important that EU keeps this technology and know-how in the EU. Please find more information in Annex 3: Case study about the sanitary industry. It also shows how adaptation to new technologies can add to Europe's competitiveness.

4.4 Economic feasibility (cost)

PVD technology is no longer more costly than traditional electroplating and can even be cheaper. Also, if investments need to be made in this industry, let them be in a future-proof technology.

Cost estimation

Cost-wise the technologies are difficult to compare. Due to confidentiality claims, it is difficult to assess what the applicants have used as cost estimation of electroplating. It is thus hard to know what the benchmark for comparison is, let alone to react on it. The balance between confidentiality and transparency is currently sub-optimal in the authorisation process and APP recommends this should be resolved in the REACH review.

¹³ Wikipedia mentions that "[...] Additional toxic waste created from hexavalent chromium baths include lead chromates, which form in the bath because lead anodes are used. Barium is also used to control the sulfate concentration, which leads to the formation of barium sulfate (BaSO₄), a hazardous waste)". Please find [here](#). Please also note the International Journal of Civil and Environmental Engineering 3:2 2011, *Treatment of Electroplating Wastewater by Adsorption Technique* by Debabrata Mazumder, Debabrata Ghosh and Pratip Bandyopadhyay. Available [here](#) and in the Annex 4.

Because of the unknowns, APP has therefore based itself on publicly available sources. On p. 29 of the Global Market Insights report¹⁴, the market size in terms of plated area (m²) and USD is given. If you divide those numbers, the result is approximately \$4.60 or €3,96 per m².

This is inaccurate because it does not take all costs of electroplating into account (and maybe assumes that only one side of an object needs to be electroplated). APP members have evidence from the market that the actual cost of electroplating per m² is at least \$30 or €25,60 per m². APP members have challenged Global Market Insights on this cost estimate, but they refused to amend the report, even when provided with above mentioned evidence.

The APP would like to point out that, if costs in the range of €3,96 per m² have indeed been used as a basis for any comparison between electroplating and PVD in the Gerhardt AfA or elsewhere, caution is needed!

On suggestion DG GROW, DG ENV and ECHA, APP has tried to compare the cost of PVD with traditional electroplating. Please see therefore the following analysis.

Table 2: Cost comparison / m²: Electroplating vs. PVD

Step in process	Electroplating	Cost	PVD	Cost	Clarifications
Base layer 1	20 µm Cu		Approx. 30 µm UV cured lacquer		
Base layer 2	15 µm Ni				
Top layer	0,5 µm Cr		0,5 µm Cr		
Material cost/m²		2.4 € (pure metal cost, in reality higher)		2.2 €, (mainly lacquering cost)	Taken is the bare metal kg price as quoted on the London Metal Exchange
Labor	Equal		Equal		Comparable for in-line systems with racking at beginning and unranking at end
Electricity consumption			Significantly Lower	Significantly Lower	
Other variable costs like chemicals, amortization, etc.				Lower	
Cost to workers health and wellbeing				Significantly Lower	Difficult to value

¹⁴ Global Market Insight Inc Statistics (2016), *Plating on Plastics (POP) Market Size & Industry Analysis, 2016 - 2023*. Available [here](#).



Environmental externalities				Significantly Lower	Not taking into account electroplating cost estimates
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The conclusion of this theoretical assessment is that PVD is cost competitive with / if not cheaper than traditional electroplating.

This is supported by the commercial reality: OEMs are already commissioning PVD treated car parts and, in [...] plant in [...] commissioned in the first part of 2017, several automotive interior parts are already produced in serial production with weekly volumes above 10,000 parts. So PVD is already proven by the market to be cost competitive with traditional electroplated equivalents.

Required investments

Gerhardi applicants claim switching would take 5 to 6 years. Moreover, in order to meet EU demand, they claim that investments of between €1.254 billion and €1.672 billion in machines and lacquer lines would be necessary.

This is a biased way of presenting the reality:

- [...] claims that if this capacity would be covered by [...] only, there would be a need for 68 metalliners and 34 lacquer lines. The total investment would in that case be € 340 Mio, which is actually substantially lower than the figure mentioned by Gerhardi. This assumption is confirmed by [...] who expect that the market can be covered by a total of 70 metalliners or equivalent hardware.
- The APP stipulates that it will take 5 to 6-year to **replace all** electroplating techniques. However, this will not happen as electroplating and PVD are likely to be used as complementary technologies.
- Applicants fail to take account the decreasing price of PVD due to **competition** between different market players on technology, lower prices and better quality. Once the regulator provides clarity, a market will be formed, demand increases, which will only happen when there is regulatory certainty and short review periods, such competition will be brought about.
- Applicants fail to recognise that PVD is an innovative technique and not a chemical process. It requires investment in **innovative hardware and in a higher skilled labour force**. While this can be seen as a cost by the OEMs, it can also be seen as part of a renewed social investment, an effort to retain/re-attract skilled workers to the EU and keeping important know-how available for Europe.
- These claims also imply that APP advocates for electroplating facilities to be closed or people being pushed out of business. This is not true! **The only request APP has it that the review period will be set at 7 years which will hopefully lead to the result that, in Europe, no new electroplating capacity will be build.** Electroplaters can also adopt PVD rather than investing in new electroplating lines.

4.5 Market feasibility (meeting demand)

PVD technology supplied by the APP members only can already meet entire market demand of PoPAA within 7 years. Consequently, it must be possible to be done quicker than that. A 12 years review period is therefore disproportional.

According to the Gerhardi applicants, PVD makers will need at least 12 years to be able to meet the market demand. However, APP members propose to reduce the authorisation to **maximum 7 years**. Counting from beginning of 2019, it would therefore be important to look at the what the capacity of the European PoPAA market is in 2026 and what the share of the market is that the APP members can supply.

For the APP, it has been extremely difficult to find reliable data for the estimation of the European market for PoPAA. APP sees two main reasons for that: i) The number of applications using PVD is still limited, as the technology is new and ii) the market data from the electroplaters are kept confidential.

This has led the APP to have to work with two scenarios':

- 1. Scenario 1:** From the [AOA](#), it can be derived that the size of the European PoPAA market can be estimated to be somewhere around **14 million m² in 2016** (for the reasoning, please see confidential [...] Annex - available on request). If the same market growth is applied as for scenario 2 (i.e. 6% per year) the market demand would in total be **25.100.000 m² in 2026**.
- 2. Scenario 2:** The APP has obtained the report "Plating on Plastics (PoP) Market Size and Industry Analysis, 2016-2023" of Global Marketing Insights, Inc. p. 152 gives an overview of the European PoPAA market which shows that the size of the European PoPAA market is **26.900.000 m² in 2016** and, applying the same growth rate, estimates that market to be **48.200.000 m² in 2026**.

From one of the APP members: As a secondary reality check, we took published consumption rates of chromium trioxide world-wide, and compared them to world-wide vehicle production, and then calculated the amount of chrome plating that would need to be on each vehicle. It seemed to match the Global Market Insights estimate, so that gave us confidence in their numbers.

APP invites the applicant to provide further data on the size of the relevant market and is willing to review its assumptions based on that.

An internal (and confidential) market investigation from the APP members, leads to the following overview of capacity vs. market demand in 2016 and in 2026 (being 7 years after 2019), set out both for scenario 1 and scenario 2:

Scenario 1

YEAR	Ionbond	Hauzer	Oerlikon	Kolzer	VTI	Total APP capacity	Total Demand	APP share of total demand
2016	[..]	[..]	[..]	[..]	[..]	1,44	14,0	10,29
2017	[..]	[..]	[..]	[..]	[..]	2	14,8	13,51
2018	[..]	[..]	[..]	[..]	[..]	2,2	15,7	14,01
2019	[..]	[..]	[..]	[..]	[..]	3,3	16,7	19,76
2020	[..]	[..]	[..]	[..]	[..]	6,2	17,7	35,03
2021	[..]	[..]	[..]	[..]	[..]	10,6	18,7	56,68
2022	[..]	[..]	[..]	[..]	[..]	17,3	19,9	86,93
2023	[..]	[..]	[..]	[..]	[..]	25,4	21,1	120,38
2024	[..]	[..]	[..]	[..]	[..]	34,5	22,3	154,71
2025	[..]	[..]	[..]	[..]	[..]	44,2	23,7	186,50
2026	[..]	[..]	[..]	[..]	[..]	54,8	25,1	193,23

Scenario 2

YEAR	Ionbond	Hauzer	Oerlikon	Kolzer	VTI	Total APP capacity	Total Demand	APP share of total demand
2016	[..]	[..]	[..]	[..]	[..]	1,44	26,9	5,35

2017	[..]	[..]	[..]	[..]	[..]	2	28,5	7,02
2018	[..]	[..]	[..]	[..]	[..]	2,2	30,3	7,26
2019	[..]	[..]	[..]	[..]	[..]	3,3	32,0	10,31
2020	[..]	[..]	[..]	[..]	[..]	6,2	34,0	18,24
2021	[..]	[..]	[..]	[..]	[..]	10,6	36,0	29,44
2022	[..]	[..]	[..]	[..]	[..]	17,3	38,2	45,29
2023	[..]	[..]	[..]	[..]	[..]	25,4	40,5	62,72
2024	[..]	[..]	[..]	[..]	[..]	34,5	43,0	80,23
2025	[..]	[..]	[..]	[..]	[..]	44,2	45,5	97,14
2026	[..]	[..]	[..]	[..]	[..]	54,8	48,2	113,92

This leads to the conclusion that APP would meet market demand already somewhere in 2022 under scenario 1 and in any case, in 2026 under scenario 2. That is within the 7 years review period that the APP asks for.

It is important to understand that these are very conservative conclusions. Several considerations need to be considered:

- **APP represents only 5 PVD providers.** In Europe alone, the APP members know of at least 10 but maybe 20 other competitors that are not members of the APP (Impact Coatings, Nanogate, Green Coat, Safe Demo, Silcos, Vacumetal, Creavac, Europ Coating, Varioplast, VTD, VaporTech). Not counting non-EU (i.e. Chinese) competitors, the case could therefore easily be made that **market demand could be covered 4 times faster.**
- **The above is based on what APP member are actually planning today. This is business planning under a challenging regulatory environment (no decisions, 12-year review periods, etc.). Should this change, what APP is advocating for, then APP members can scale up their production much quicker than is indicated in the above statistics.**

- It is also important to understand that meeting market demands will result in **fierce competition which will have a drastically lowering effect on price and will significantly increase of quality and applicability**. PVD technology will therefore also become an export product, allowing EU SME's to thrive on a global market.

Please be also referred to Annex 6: APP presentation on the PVD market and market developments as shown on 6 September at the meeting with DG ENV, DG GROW and ECHA.

4.6 Consistency with EU policy at large

A decision to apply a 7 years review period of the Gerhardi AfA is entirely consistent with all EU Policy. A decision to apply a 12 years review period of the Gerhardi AfA is entirely inconsistent with all EU Policy.

It is important for the European Commission to be consistent. Taking quicker decisions on Gerhardi, Lanxess and Hapoc and shortening the review period of Gerhardi from 12 to 7 years, would be consistent with all of the below mentioned EU policies whilst maintaining 12 years review period would be contradictory to all of the below mentioned EU policies.

- **Compliant with/and in the spirit of REACH:** This needs little explanation and follows from the whole manifest but the PVD technology does not use any SVHCs or substances that are considered to have endocrine disrupting properties. Chromium or other metals used in PVD technology are zero valent and therefore **harmless for human health**. It therefore ensures a high level of protection of human health [...] while enhancing competitiveness and innovation.
- **OHS – legislation and workers protection:** PVD surface treatment technologies ensures the highest level of workers protection, as the polymerisation process does not have any occurrence of toxic unhardened resins and is fully automated in the vacuum chamber inside a grey room atmosphere with advanced air ventilation technology. The closed system protects workers from exposure to the materials. Additionally, there is no danger existing for OEM personnel, since the delivered products are not containing any hexavalent chromium.
- **Resource efficiency:** The PVD technology allows for a significant reduction in the amount of raw materials used compared to traditional coating techniques. The thickness of electroplating layers is around 20-30 microns, instead PVD layers usually are less than 0,5-1 micron to give an idea of the differences.
- **Recyclability:** The PVD technology is vacuum based and free of any gaseous or solid waste. Any residual materials can be completely recycled or disposed of as standard metal waste. **Lacquer, PVD and plastic are recyclable without need to decoat**. PVD technology is therefore compliant with the requirements of Directive 2000/53/EC – the End of Life of Vehicles Directive. Moreover, PVD technology significantly reduces the toxic waste from emissions of solvents i.e. volatile organic carbon (VOCs). The off-gases resulting from the process only contain small volumes of VOC, which are below legal limits, and which can be eliminated by post-combustion. All APP members are currently exploring means to replace VOCs by 100% solid content of the UV coatings. PVD coated parts do not contain lead, mercury or cadmium which makes them easier to recycle.

- **Waste management and water consumption:** PVD does not use water in their production process, meaning that the risk of contamination is eliminated and that PVD operations can always run regardless of the availability of water (due to drought or otherwise). Electroplaters on the other hand use at least 40.000 m³ of water every day in their production processes. The water is cleaned afterwards but cannot be reused because of particles remaining.
- **Less energy/less CO²:** The PVD process uses a plug and play system, which means it uses up to 5 times less energy than comparable traditional coating technologies. It therefore releases up to 5 times less emissions compared to electroplating systems. Energy consumption is reduced due to a very fast curing time in seconds (<30 sec) instead of minutes for thermal curing lacquer systems (~30 min oven drying at 80°C). In comparison, the electroplating process is much less efficient. Just for the metallization process, there is an energy consumption of about 28-42 kWh/m² for the Cu-Ni-Cr process. The PVD layer is applied with energy consumption of about ~4,7 kWh/m². This is in line with the Commission's strategy for long term EU greenhouse gas emissions reductions, the Paris Agreement etc.
- **Key Enabling Technology:** Key Enabling Technology (KET) are identified in the “European strategy for Key Enabling Technologies – A bridge to growth and jobs”¹⁶. These technologies are knowledge intensive and associated with high R&D intensity, rapid innovation cycles, high capital expenditure and highly-skilled employment. Should PVD technology be earmarked as KET?
- It will also help **EU Policies on road safety and autonomous driving** set out in the Communication on Connected and Automated Mobility (CAM), May 2018, see [here](#) and the European Parliament INI Report on Connected and Intelligent Transport Systems (C-ITS), February 2018, see [here](#) and the upcoming Commission delegated regulation on Intelligent Transport Systems which will mainly deal with the communication between vehicles and infrastructure, and interoperability.
- **The EU's renewed EU Industrial Policy Strategy**¹⁷ sets out ambitions/priorities for the EU to investing in a smart, innovative and sustainable Industry: this is about PVD much more than it is about electroplating.

¹⁵ Study by the Landesamt für Umweltschutz (environmental agency) in 2003 in cooperation with Zentralverband Oberflächentechnik e.V. (Germany's central organisation for surface technology).

¹⁶ COM(2012) 341 Communication from the Commission “European strategy for Key Enabling Technologies – A bridge to growth and jobs”, Brussels, 26.6.2012. Available [here](#).

¹⁷ COM(2017) 479 Communication from the Commission “Investing in a smart, innovative and sustainable Industry: A renewed EU Industrial Policy Strategy”, Brussels, 13.9.2017 see [here](#).

5. Conclusion

On p. 77 of the AoA, the applicants conclude on the 12 years review period claim by summarizing the key points. To conclude, and building on what has been set out in this manifest, APP refutes each key point (in bold):

- *Based on experience and with reference to the status of R&D programs, implementation of feasible alternatives for pre-treatment and plating process for key PoPAA applications is not foreseen to be finalised within 12 years after the sunset date (Chapter 8);*

This is not true today: Implementation of PVD is today already possible.

- Any potential alternative is required to pass full qualification, certification and implementation/industrialisation to comply with demanding standards in the automotive sector and their customer (Chapter 5);

Correct but PVD has passed already such qualifications, as demonstrated in this manifest and articles have been processed already with PVD. These parts are certified and industrialized in line with the demanding automotive standards.

- *The European automotive industry in general requires optimal framework conditions in order to maintain its competitiveness, its high technological standards and to preserve/generate jobs;*

Correct but PVD has already been proven since over 20 years that it satisfies this demand of the EU automotive industry for high technological standards and competitiveness.

- *Average life cycles of an automobile model is about 22 years, comprising 3-5 years development time, 7 years of production and at least a 10-year service life, during which there is a need to guarantee availability of spare parts. With regard to both the highly complex nature of supply chains and the lifetime of vehicles, planning reliability is crucial (Section 5.2.1.);*

Not true (anymore). For automotive parts with a decorative function technology change in much shorter cycles. As an example, [...] used electroplated door locks, went to DLC-coatings (PVD) for their lower friction, switched back to a different process including electroplating and kept still high-end products with DLC coatings.

- *Even assuming the CrVI alternative (etching pre-treatment and main treatment) would be ready to be implemented instantly, more than 12 years would be required until the complete elimination of Cr(VI) (Chapter 5);*

This reasoning is flawed. The statement that more than 12 years might be required until the complete elimination of CrVI might be true (as APP mentioned in the manifest: electroplating and PVD are likely to be used as complementary technologies for a long time). It is no reason, however, not to do anything now and a review period of 7 years leads to getting there earlier and stops new electroplating capacity from buying build / supported. Electroplaters can also adopt PVD rather than investing in new electroplating lines.

- *The socio-economic impacts for all non-use scenarios as calculated in the SEA outweigh potential health impacts correlated with continued use of PoPAA at least by a factor of 140:1. Considering the worst-case exposure levels provided in the CSR and the resulting worst-case health impacts of EUR 36,409 expected per*

site until 2029, a long review period that allows step-wise implementation of upcoming alternatives should be granted.

It is audacious to calculate the value of health in EUR – let alone the value of wellbeing and APP would not want to go there. And it does not have to as PVD technology is a future-proof alternative without risk for workers' health and wellbeing.

As a consequence, a review period of not less than 12 years is selected because it coincides with best case estimates by the applicants of the schedule required to industrialise alternatives to chromium trioxide.

This conclusion of the applicant is not valid anymore today. This manifest demonstrated that PVD has developed to be a technically and economically feasible alternative that can provide market demand within a 7-year period.

Concluding, the APP hopes that the the Reach Committee will take the new information laid out in this manifest into account when formulating a final decision, in accordance with the principles of EU policy making and more particularly the guidelines on better regulation.¹⁸

As can be seen from the manifest, most of the information regarding PVD in the 2016 Opinion is outdated, some information is also disputable. The APP would find it reasonable and proportionate - also given the significant difference in capacity and resources of the APP members compared to those of the applicants and their supporters – that the burden of proof would be shifted to the applicants. If the electroplating case is good, it can be better made again in 7 years' time than 12.

This would align with the [Minority Position](#) of Jean-Marc Brignon (please find figure 3) and the [Minority Position](#) from Simon Cogen, Maria Noring and Lars Fock (please find figure 4).

Figure 3: Minority Position Jean-Marc Brignon

Overall I do not agree with granting a long review period for this application, because I think there is an uncertainty about the timeframe of availability/acceptance of alternatives by the market (by final customers and therefore by OEMs), and a lack of information and justification in the AfA on that alternatives (especially Cr III) could not be available during the normal review period.

Figure 4: Minority Position Simon Cogen, Maria Noring and Lars Fock

¹⁸ Activities of the EC should be evidence based: meaning they are based on the best available evidence including scientific advice, or a transparent explanation of why some evidence is not available and why it is still considered appropriate to act (p. 7 of the [Better regulation "Toolbox"](#)).

3. Customer acceptance

The applicant places a lot of importance on customer acceptance arguments. So much so that we would have expected market surveys and customer demand studies supporting the claims made. Such an analysis could have informed SEAC whether customers are ready to accept changes and over which timeframes (depending on which types of vehicles, market segments and parts). While there is a lot of technical and economic information on alternatives, there is nothing that properly justifies the applicant's claims that customers would not accept parts made with alternatives to chrome(VI).

The above-mentioned arguments clearly show that a 12-year review period is not justified and a 7-year review period should be granted instead.

Considering all of this and building onto the discussions held on 6 September with DG GROW, DG ENV and ECHA, the APP humbly requests the Reach Committee to:

- **Shorten the review period of Gerhardi to maximum 7 years.**
- **Speed-up the decision-making process on Gerhardi and Lanxess applications by autumn 2018.**

Thank you for your support.

Signed in Brussels on 14 September 2018

Alliance of PVD Providers

IHI Hauzer Techno Coating B.V.
Ionbond Netherlands B.V.
Kolzer SRL
Oerlikon Balzers Coating Germany GmbH
Vergason Technology, Inc



6. Annexes



Annex 1: An APP plea “Regulate to make OEMs change to alternative technologies”

Please find below the un-edited arguments for a quick decision and shorter authorisation period, coming directly from one of the members of APP, perfectly highlighting the aforementioned lose-lose situation and the catch 22 in which this file finds itself and that needs to be resolved:

A. Today PVD technology is competitive with hexavalent chromium plating for coatings on automotive plastics with a decorative character.

B. Regulation is necessary to enforce OEMs to make a change in the direction of alternative technologies, even if these technologies are competitive to hexavalent chromium plating. Therefore, the market will not ask for any changes if there will be a long authorisation period.

From the point of view of a responsible OEM-manager using products, plated with Cr⁶⁺ plating technology following arguments will prevent a change in chosen technology:

- 1. There is no danger existing for your own personnel, since the delivered products are not containing any hexavalent chromium.*
- 2. The existing electroplating technology, using hexavalent chromium, is working as specified and is proven since decades. Changing to a new technology means that risks have to be taken by the OEM due to a lack of experience with the alternative technology.*

Much work (and therefore costs) will be involved to reduce such risks to a minimum, but because of failing historical data the risks will always be higher in comparison with a long term used technology.

Following actions will be required by OEMs:

- a. In order to validate the alternative technology automotive OEMs must ensure to have own personnel with knowledge of the new technology (which includes the capabilities and limitations of the new technology) either by training or by hiring personnel form outside.*
- b. Existing specifications are based upon the validation of hexavalent chromium plating technology. These specifications need to be critically checked on their suitability for qualification of coatings produced with alternative technologies like PVD, since in different aspects the alternative technologies will have advantages as well as disadvantages. One may expect that different testing methods will be developed since the technologies are differing.*
- c. The distribution of age and career has also consequences: this [table](#) from the Central Bureau for Statistics part of the [website](#) CBS shows that more than 50% of the persons, working in industry for 10 years or more, is in the age of 45-65 years. These persons are inherently conservative in their concepts at work (which is instrumental due to the procedures within the automotive industry) and will from that perspective not actively be looking for new technologies when these will be related to additional cost and potential risks compared to satisfactory existing technologies.*

The table also shows that under the age of 45 years less than 33% of the persons will be working in industry for 10 years or more. This group may be open to new technologies, but the most ambitious persons in this group will leave before the technology will be introduced in case of 12 years authorisation.

Taking all the above considerations in 1 and 2 in mind, it is extremely unlikely that both by reasons of cost and personal career considerations any action will be taken by a responsible manager at the OEM if an authorisation period of 12 years will be granted.

Actually, cases are known already, as stated [...], that active search for alternatives has stopped immediately after the decision for a 12 years authorisation period was decided by the EC (case of Grohe, consultation number 0034-01 and 0034-02).

C. Outsourcing to China is already happening

D. Based on the expectation that hexavalent chromium as SVHC would be banned, alternative providers have already been heavily investing in technologies to replace hexavalent chromium plating technology.

These are high risk investments which will only be successful if the market (i.e. the OEMs) will accept the introduction of the new technologies. Without a reasonably fast return of investment, chances for the introduction of alternative technologies will be very limited.

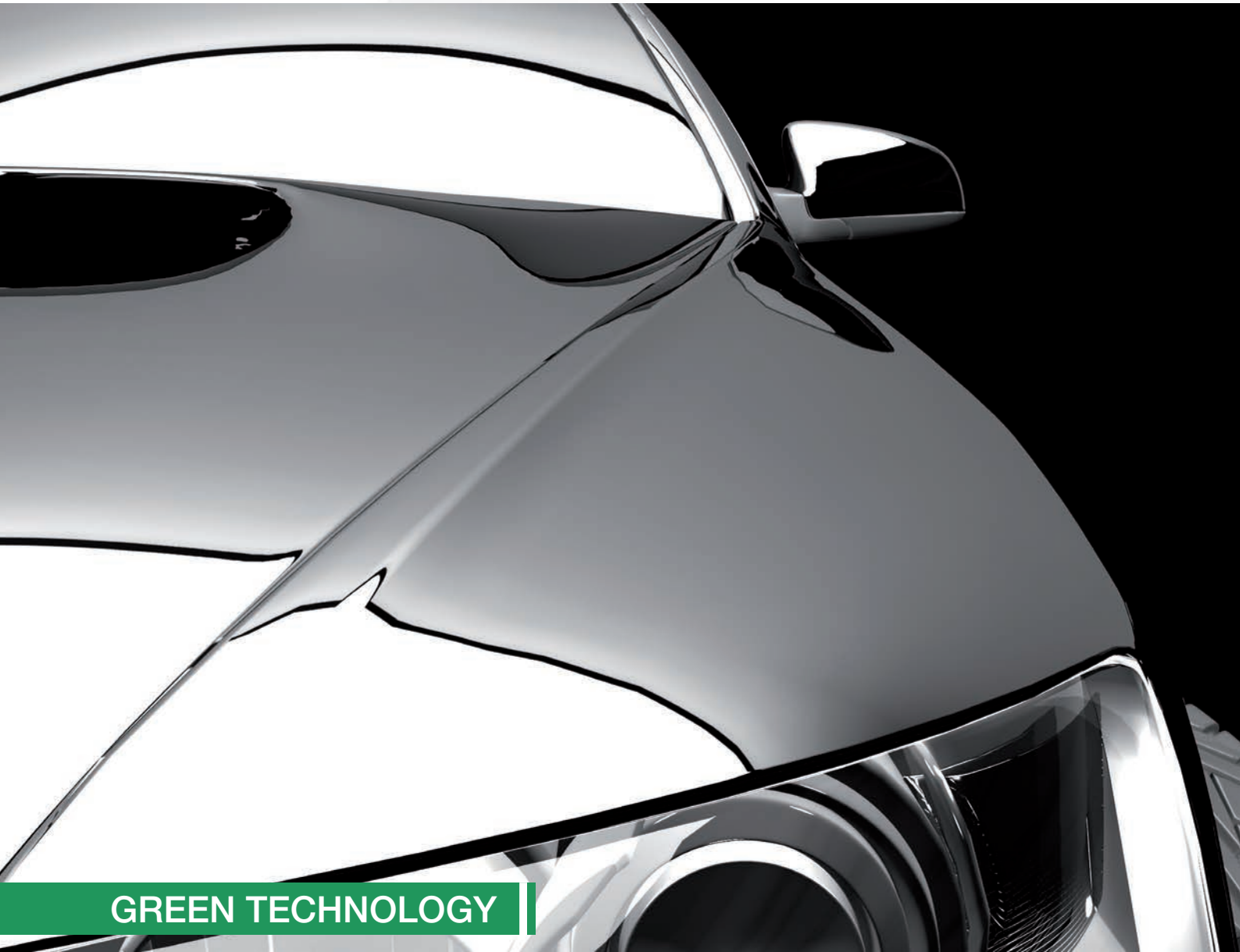
The conclusion of this APP member is simple: In case of an authorisation period of 12 years at the end of that period the situation will still be unchanged: new alternatives will not be made available based on today's negative experiences with taking these risks...



Annex 2: APP presentation on PVD technology versus electroplating

PVD SPUTTERING

NEW ERA OF CHROME COATING



GREEN TECHNOLOGY



PVD - PHYSICAL VAPOR DEPOSITION

Chrome plating is the ideal coating to ensure both superior mechanical performance and an attractive metallic appearance, trendy, increasing the perceived value.

To overcome the limits of traditional chromium plating, **Kolzer** developed CLEAN CHROME PLATING by vacuum sputtering technology.

This process adopts a physical and not a chemical process, therefore eliminating any harmful emissions.

The performance benefits are considerable:

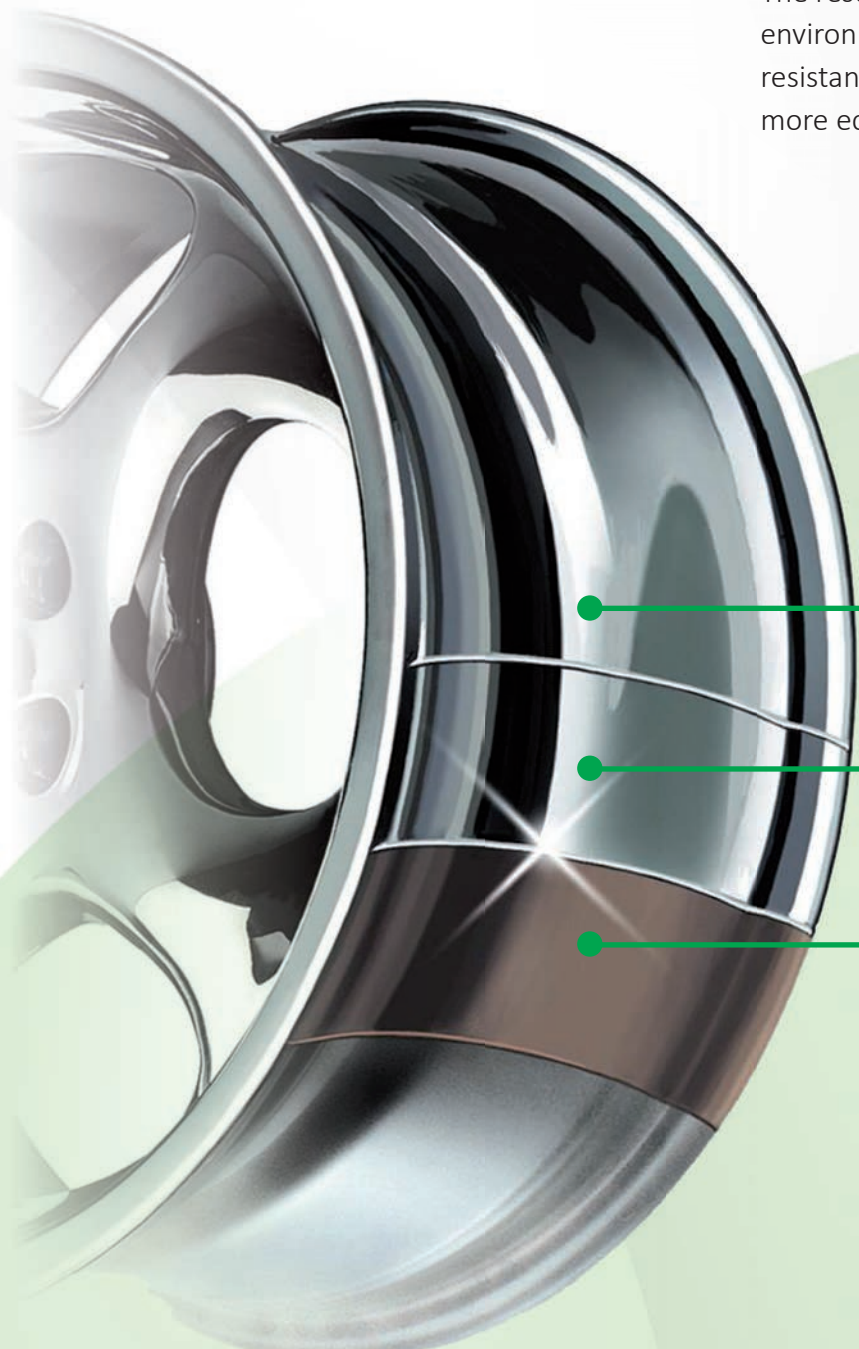
environmental: clean process at room temperature, without water, totally free of chemical emissions

aesthetic: brilliant metallic finish, vast array of colors and polish variations

functional: durable, high hardness, abrasion and corrosion resistant

productivity: extremely economical and short machine cycles, high repeatability, diminished imperfections.

The result, **Kolzer PVD** machines produce environmentally friendly pieces that are more resistant and therefore make end use products more economical.



TOPCOAT UV varnish (optional):

It provides protection to the metal layer and increases its performance

METAL PVD:

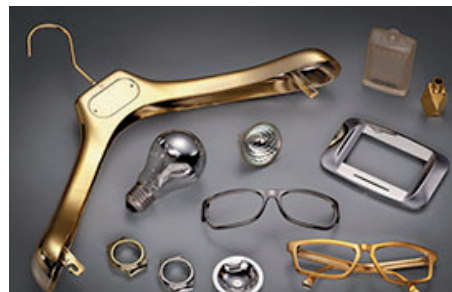
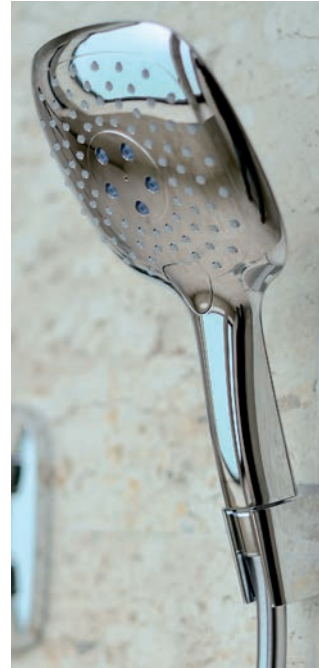
Any metal or alloy: Stainless Steel, Chromium, Titanium, Copper, Brass, Silver, Aluminium, Nickel-Chrome and many others

BASECOAT UV varnish (optional):

It seals and improves substrate hardness. It levels eliminating imperfections, improves adhesion and provides brightness

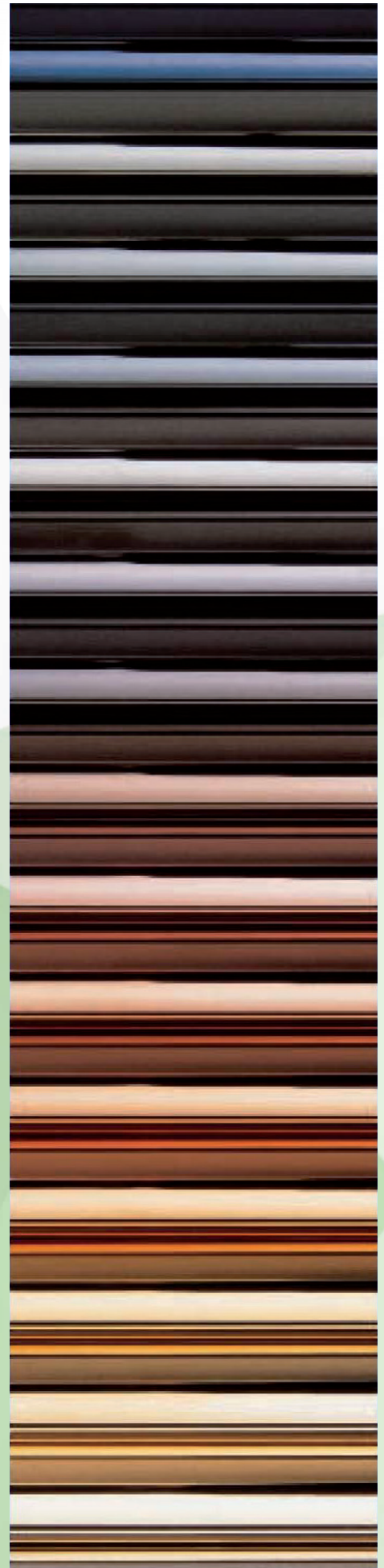
PVD APPLICATIONS

- Automotive
- Home Appliances
- Packaging
- Lighting
- Bathroom fixtures
- Fashion
- Design



PVD BENEFITS

- Environmentally friendly
- Uniform deposition
- Low temperature
- Repeatable
- Multilayer
- Adjustable thicknesses (semi-transparent, full coverage, high thickness)
- Clean Chrome
- No harmful waste
- Functional capacities: transparency to RF, EMI shielding, semi-transparency
- Vastly quicker production time when compared to traditional toxic chrome plating
- Small production footprint
- Minimizes the need for outsourcing
- Maintains the elasticity/flexibility of the piece
- Any material can be coated
- Greater flexibility in the design of the pieces
- Wide range of finishes: colours and brightness, glossy and matt
- Large variety of substrates
- Recyclable





CRITICAL FACTORS FOR SUCCESS

Substrates have added **resistance to**

- humidity
- thermal shocks
- chemical agents
- corrosion
- impact
- abrasion
- weathering

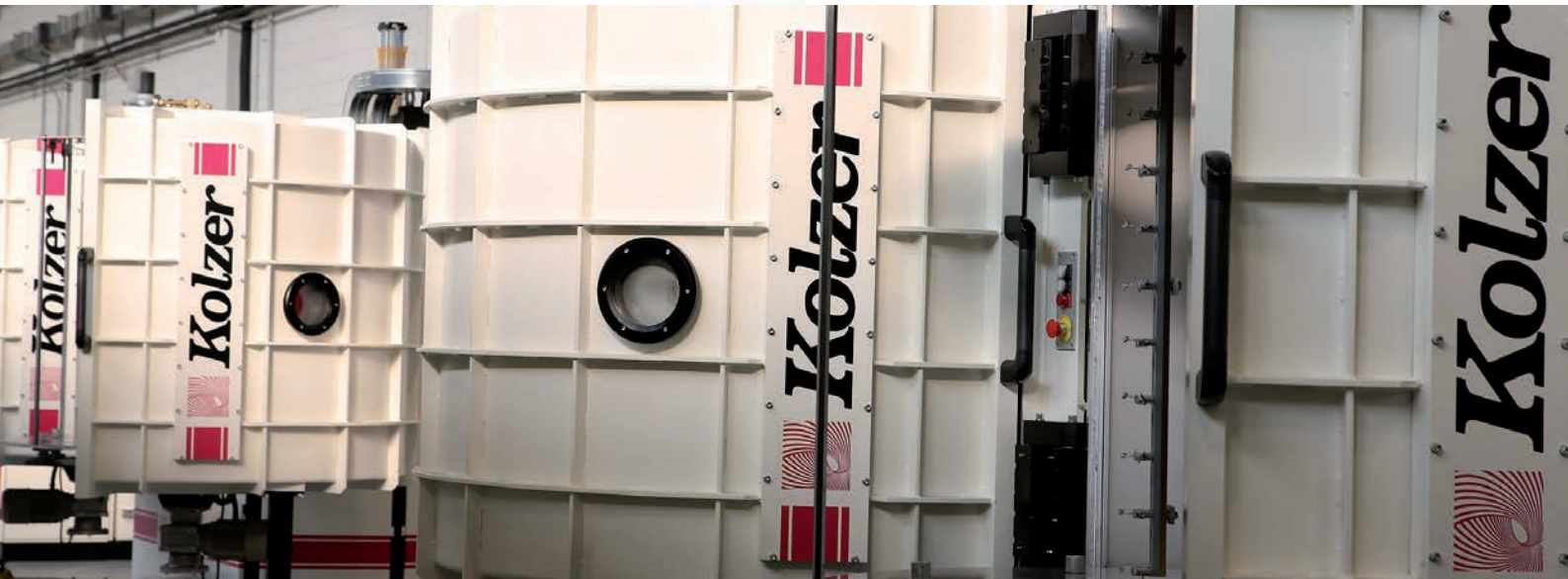
The **process cycles** are **very fast**, with an extraordinary efficiency resulting in an economical “**green**” **production**.

The UV + PVD combination is **safer**, more **economical** and **environmentally friendly** than electroplating.

It requires just a **few steps** and passes the toughest **OEM requirements**.

It enables engineers and designers to have **greater flexibility and choice** in product **design**.

PVD PLANTS



The Kolzer machines are simple to use and provide advanced PVD sputter coating results. They are automated, digitised and even remotely manoeuvrable. The machine integrated with an UV painting line, offers high volume production in a pressurized chamber, in line with the customer's specifications and with diminished production waste.

The history of the production cycles are saved automatically, allowing their recall and execution at any time. They allow full control of the production line: the process parameters and recipes are provided by Kolzer. The remote service allows access to process controls, managing and loading new parameters.

DGK36"



All User Friendly **Kolzer PVD Technology** has a facilitated "**price entry**".

The DGK model allows to have an excellent coating result with very fast cycle times. The machine is supplied with dual loading trolleys to facilitate loading and unloading. These can be easily integrated within the UV coating plant.

MK63"



The MK machine is a symbol of innovation, practicality and design. By dual loading and unloading, manual or automatic directly on the doors to the ease of use of the Windows software, the entire production cycle is fast and free of complexity.

This vertical PVD Sputtering plant offers a PVD Plasma PECVD technology "combined" into a single machine, able to achieve maximum flexibility and creativity.

ENJOY PVD TECHNOLOGY

Kolzer offers qualified Engineering for the supply of equipment, from the “compact productivity station” for small and medium-sized companies, to special plants and in line processes for high volumes or articles of large dimensions.

Why a PVD sputtering KOLZER plant?

- Great service efficiency through ease of loading/unloading and low maintenance
- Massive production by maintaining a low power and materials consumption
- Plasma, PECVD and PVD sputtering processes available on all plants
- Steel machined chambers, designed and manufactured to last over time
- Global network of Consultancy, assistance and prompt after-sales service
- 2 years guarantee and minimum guaranteed working life of 12 years
- Windows operating system with Internet 24/7 service
- The fastest certified cycle times on the market
- More than 1,000 plants installed worldwide
- High productivity with a single operator
- Totally “Eco-friendly” processes
- Space-saving design

Low operating costs and faster production cycles currently available on the global market, ensure the KOLZER machines the highest industry standards, at the most competitive costs.





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Annex 3: Case study about the sanitary industry



Please find below a case study from mid-90s regarding the sanitary industry.

It demonstrates that PVD technology is not new. It would not be the first time PVD would successfully replace electroplated substances and it shows how allowing for a technology in one sector will also create positive cross-fertilisation to other sectors like the OEM sector in which this technology is already approved and used:

In order to replace cyanide-based solutions during electroplating, largely the same consortium of PVD coaters have met the request from the sanitary industry to replace electroplated brass by PVD ZrN for the sanitary industry (bathroom faucets and fixtures) over a period of approximately 5 to 7 years.

In spite of industry claims to the contrary, the ZrN material turned out to be much more wear resistant than the original brass. Color uniformity and reproducibility was improved tremendously.

The PVD finishes turned out to be a design advantage over electroplating as electroplating has the tendency to grow coatings with a so called "T-bone" effect. The edges get a much thicker coating than the flat surfaces. That T-bone effect creates a lot of issues with staying in tolerance of tight fit components.

Based on that success, the OEMs further utilized the PVD technique to expand their finishes and offerings, like Nickel, black, Oil Rubbed Bronze, and stainless steel.



Annex 4: Treatment of Electroplating Wastewater by Adsorption Technique

Treatment of Electroplating Wastewater by Adsorption Technique

Debabrata Mazumder, Debabrata Ghosh and Pratip Bandyopadhyay

Abstract—The wastewater treatment process was evaluated in an Electroplating unit that practiced chrome and bronze plating. With a view to recycle and reuse the wastewater, adsorption process was adopted as single stage treatment instead of the existing chemical methods. Wastewater was collected from chrome and bronze plating unit and analyzed for the relevant parameters. On the basis of characteristics, adsorption process was selected and materials such as wood charcoal, coconut shell carbon, activated carbon etc. were not proved to be effective for acceptable removal of chromium and copper as well as colour. Later, Activated Alumina (AS 37 of grain size 0.6 mm – 0.9 mm) was opted and its performance was examined by several batch and column studies. The results showed that the chrome and bronze plating wastewater might be combined together and the composite sample could be treated with Activated Alumina to remove chromium, copper and colour appreciably. Under the existing pollution load in terms of chromium and copper, an adsorption column made of activated alumina was designed following the classical Bed Depth Service Time (BDST) relationship.

Keywords—activated Alumina, adsorption, chrome-bronze plating, electroplating wastewater

I. INTRODUCTION

THE growth of civilization needs the manufacturing of materials, which are resistant to corrosive environment. Chrome and Bronze plating are two such methods to ensure longer durability of metallic substances. Such electroplating units have potential to generate the effluent consisting of heavy metals like chromium, copper, zinc, cadmium etc. The toxicity of the effluent obviously depends on the concentration of the respective metals as well as duration and type of discharge. With the increasing use of variety of heavy metals in electroplating industry problem may arise from potential toxicity in the environment to a great extent. Chromium is an essential element needed for human and other living organisms, which primarily involves in the action of insulin in glucose metabolism and helps transport of amino acids into the heart and liver. Its deficiency may disturb carbohydrate, lipid and protein metabolism [1].

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Water containing 0.5 mg/l or more chromium is considered highly toxic because it has carcinogenic and mutagenic properties [2]. Similarly copper is also an essential element of several proteins and enzymes. Deficiency of copper causes demineralization of bones, anemia, fragility of arteries, discoloration of skin as well as hair. High concentration of copper (above 3.0 mg/l) in water may lead to accumulation of copper in liver and lenticular nucleus of brain. Ultimately it may cause hepatic cirrhosis and brain necrosis. Renal damage may also occur due to accumulation of copper in kidney by means of consumption of water with high copper concentration in excess of permissible limit [1].

Faust and Ali (1987) [3] ascertained that removal of Cr^{+6} is extremely low while using Powdered Activated Carbon (PAC) in the pH range of 6.8 to 8.3. Tewari *et al.* (1989) [4] had shown that adsorption of chromium and copper reached to peak value at pH 5.5 and 8.0 respectively when activated carbon was used as an adsorbent. Shukla and Moitra (1994) [5] observed that acid charred waste of an oxalic acid manufacturing plant was capable of removing 98.6% of copper in 3 days. Bentonite immobilized in a polymer matrix of polysulfone in the form of special beads was effectively used in a column for the removal of copper [6]. Copper removal was possible from synthetic aqueous solution containing 5.0 to 100 mg/l of Cu^{+2} concentration using low grade rock phosphate [7]. Rice straw showed appreciable adsorption capacity than saw dust for the removal of Cr^{+6} and it could be used for the removal of the same in plating industry. In that study, at a pH 2 the maximum removal of chromium was around 95% [8]. Copper from wastewater was removed by using fly ash, with the efficiency of 62% and 98% at 60 mg/l and 2 mg/l copper concentration respectively [9]. Schmuhl *et al.* (2001) [10] established the effect of *chitosan* on adsorption of Cr^{+6} and Cu^{+2} and observed that Cr^{+6} removal was highest at pH 5.0 but pH did not affect the removal of Cu^{+2} . In presence of acidic pH ranging between 4 and 5.5 the “RAR” soil with greater amounts of exchangeable Aluminium and Iron oxides showed a low adsorption capacity but a high affinity for Cu^{+2} [11]. Aslam *et al.* (2004) [12] observed that the solution pH did not have a significant effect on the removal efficiency during adsorption of copper in sand.

The potential of mesoporous materials with MCM-41 type structure functionalized with different ratios of aminopropyl groups, namely Na_{50} , Na_{25} and Na_5 in removing nickel and copper from industrial electroplating wastewaters was evaluated. The observation revealed that reactive

aminopropyl-Si MCM-41 and similar materials could be used as a promising and alternative environmental technology in the future [13]. A batch study was conducted to remove hexavalent chromium (Cr^{+6}) using scrap iron filings in both synthetic wastewater, containing 30 mg/L of Cr^{+6} , and chromium plating wastewater. Optimum condition for removal of Cr^{+6} was found to be at pH 3, iron particle sizes (35 – 200) mesh, agitating rate 250 rpm, contact time 180 minutes and iron dosage of 1 g. It was also observed that nickel and copper in the aqueous solution did not affect on the reduction of hexavalent chromium [14].

In order to purify electroplating wastewater with respect to Cr(VI) the adsorption behaviour of amorphous aluminium oxide was studied under batch method. With a varying Cr(VI) concentrations in the range of 10 to 200 mg/l, Langmuir model was found to best, showing a maximum adsorption capacity of 78.1 mg/g. Amorphous aluminium oxide also showed a high adsorption capacity in case of purification of Cr(VI) bearing electroplating wastewater [15]. A study on Fluidized zero-valent iron (ZVI) process was conducted to reduce hexavalent chromium (chromate, CrO_4^{2-}) to trivalent chromium (Cr^{3+}) from electroplating wastewater. ZVI process was selected because of (i) extremely low pH (1–2) in electroplating wastewater, (ii) production of ferric ion from the reaction of Cr(VI) and ZVI that can act as a coagulant to assist the precipitation of $\text{Cr}(\text{OH})_3(\text{s})$ and (iii) higher ZVI utilization for fluidized process due to abrasive motion of the ZVI. In this study Fe^{2+} was considered as an indicator for complete reduction from Cr(VI) to Cr(III) [16].

In the present study an Electroplating unit employing chrome and bronze plating was selected for process evaluation, removal of copper and chromium from wastewater and exploring the scope of recycling. The chemical treatment was planned to be replaced by physico-chemical process like adsorption. The wastewater emanated from bronze and chrome plating units were mixed together to prepare a composite wastewater sample. Later, activated alumina (AS 37 of size 0.6 mm - 0.9 mm) was utilized as an adsorbent for the removal of copper and chromium present in the composite wastewater. The study revealed that activated alumina performed very well as the adsorbing media for the removal of both chromium and copper.

II. ELECTROPLATING UNIT UNDER THE PRESENT STUDY

The Study was performed with the effluent from rinsing tank of electroplating plant of M/s. Jessop & Co. Ltd., Kolkata, India.

A. Plant description

M/s. Jessop & Co. Ltd., Kolkata was founded in 1788 and now it is engaged in the manufacturing of EMU Coaches, Wagons, Road Rollers, Cranes and Mining equipments. The plating operations, i.e. chrome plating and bronze plating are conducted for mining components. The components, susceptible to wear and tear, are chrome plated, whereas the components exposed to corrosive atmosphere are bronze

plated. The average monthly requirement of such plated components (as needed in India's mining industry) is approximately 50,000 sq. ft per month. M/s. Jessop & Co. Ltd. manufactures about 6000 sq. ft. of plated items per month out of which 2500 sq. ft. is chrome plated and 3500 sq. ft. is bronze plated.

B. Existing treatment unit

The existing treatment unit follows chemical treatment to abate the heavy metal pollution arising out of chromium and copper. When appreciable sludge accumulation occurs in the rinsing bath, the entire rinsing water is changed and the wastewater is drained out to the equalization tank for treatment. Sodium meta-bi-sulphite is added to promote conversion of Cr^{+6} to Cr^{+3} under pH range around 4.0 to 4.5. The wastewater from rinsing bath used for bronze plating is also drained out into another equalization tank when found unsuitable. The wastewater in the equalization cum storage tank contains CN^- , which is firstly made alkaline with Sodium hydroxide and then Sodium hypochlorite is added for cyanide destruction. As a result, cyanide is converted to cyanate and finally to CO_2 and N_2 , when pH is raised to above 7.5. The primary treated wastewater from both the tanks is mixed together in a separate neutralization tank for leveling the pH fluctuation. Then the neutralized wastewater comes to the clarifier and the settled solids are dewatered in a pressure filter. Solid wastes are sealed in a container for safe disposal and the effluent is discharged to the municipal sewer. The flow diagram of existing chemical treatment of the electroplating wastewater is shown in Fig. 1.

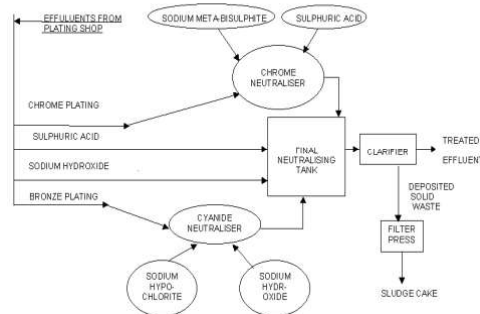


Fig. 1 Flow sheet of existing wastewater treatment unit

C. Effluent Discharge Standards

In India the effluent discharge standards are laid down and monitored by Central Pollution Control Board, New Delhi, which is a statutory agency of Ministry of Environment and Forests, Government of India. The standards specify the desirable quality of effluent emanated from various industries. In case of Electroplating industry, the discharge standards for hexavalent chromium (as Cr^{+6}), total chromium (as Cr) and copper (as Cu) are mentioned as 0.1, 2.0 and 3.0 mg/L

respectively [17].

D. Major source of waste generation

The rinsing of material after plating operation is required to remove any plating bath solution that may be left on material. Rinsing operation emanates the largest volume of wastewater from metal plating operations. Rinse waters finally become contaminated with varying concentration of heavy metals as per the type of rinsing scheme.

The tank capacity of rinsing bath was measured to be 4000 litres for both the chrome and bronze plating. Usually, the wastewater was discharged after a month period with an amount of (4000 + 4000) i.e. 8000 L. The plating bath liquid is changed occasionally when sufficient sludge is accumulated at the bottom. At this stage, the bath liquid is pumped and the sludge is removed. After cleaning operation, the bath is again filled with liquid that was kept aside. The appropriate bath composition is maintained by adding necessary amount of chemicals.

The chemical composition of Chrome plating bath and Bronze plating bath and current passed through them are as follows.

Chrome plating bath

- (1) Chromic Acid : 220 to 250 g/L
- (2) Sulphuric Acid : 1 in 100 ratio.
- (3) Current : 300 amps/sq. ft.

Bronze plating Bath

- (1) Bronze Salt A : Bronze Salt B in the ratio of 130 : 60 to keep the concentration of Copper (Cu^{+2}) : 26 – 32 g/L and Tin (Sn^{+2}) : 18 – 22 g/L.
- (2) Potassium Cyanide is added to get CN^- concentration 30 – 38 g/L. Potassium Hydroxide is also added with a concentration 4 – 8 g/L
- (3) Current : 25 amps / sq.ft.

III. EXPERIMENTAL

A. Materials

Activated Alumina of AS-37 grade with grain size 0.3 – 0.6 mm was used as adsorbing media, which was supplied by M/s. Oxide India Pvt. Ltd., Durgapur, West Bengal, India. Triple distilled water was employed for preparation of reagents whereas ordinary distilled water was used for other analyses. Initially, the wastewater volume generated from various major sources was noted and rinsing bath of both the chromium and bronze plating was found to be the principal source. Therefore, samples were collected from the respective rinsing baths and analyzed for the relevant parameters. To accomplish the simultaneous removal of copper and chromium, the chrome and bronze plating waste streams were mixed together to make a composite sample. The usual discharge of wastewater from chrome plating bath was 4000 L per batch and the bronze plating bath also discharged almost same quantity. Therefore, the mixture of two, i.e. composite

wastewater should contain wastewater from both the baths in 1 : 1 ratio. The total volume of wastewater in the composite bath was 8000 L. The composite wastewater sample was allowed to flow into the adsorption column with different flow rates, adjusted by the peristaltic pump.

B. Method of analyses

All the parameters were measured according to standard procedures suggested by Standard Methods (1985)[18] and Jeffery *et al.*, 1989 [19]. Chromium and Copper was determined by Colorimetric and Sodium Di-ethyl dithiocarbamate method respectively.

C. Characterization of wastewater

The wastewater collected from the rinsing bath of the Chrome and Bronze Plating unit were analyzed for the relevant parameters. A composite wastewater (1:1 Chrome and Bronze plating wastewater) was also analyzed.

D. Batch adsorption study

A batch study was performed with varying dosages of activated alumina (10, 20, 30, 40, 50 and 60 gm/L) in 100 ml of composite wastewater collected in the second phase and for the batch periods of 10, 20, 30, 40, 50 and 60 Min. Another study was carried out to determine the equilibrium concentration for the sorption of Chromium and Copper using Activated Alumina of dosage 50 g/L. 100 ml portion of the composite bath wastewater containing 13.6 mg/L of Chromium and 3.4 mg/L of Copper was added with the above dosage of Activated Alumina and was allowed for shaking for contact periods of 5, 10, 15, 30, 45 and 60 Min. Thereafter, effluent was centrifuged and the supernatant was analyzed for Chromium and Copper.

E. Isotherm Study

Isotherm study was performed with different dosages (10, 20, 30, 40, 50 and 60 gm/L) of Activated Alumina with the optimum contact period of 45 Min. Batch Isotherm Study was carried out at room temperature (average is about 25°C) using 100 ml composite wastewater with abovementioned dosages in separate bottles. The bottles were shaken in a rotary shaker at 25 rpm for a contact period of 45 Min. Later, the effluent was centrifuged and analyzed for chromium and copper. According to adsorption kinetics of different models the data were analyzed to establish the most appropriate Isotherm.

F. Column Study

Composite wastewater was fed through the column of height 100 cm and internal diameter (I.D.) 1.5 cm by a peristaltic pump with a flow rate of 4.98 ml/Min. The wastewater after 180 Min. was collected and analyzed for chromium and copper. The bed depth of the column was provided as 25 cm, 35 cm and 50 cm. The setup of the Column study is shown in Figure 2. The influent concentration of chromium and copper was observed to be 13.6 mg/L and 3.4 mg/L respectively. Effluent samples were collected at various time intervals and analyzed for Chromium

and Copper. From the results of analysis a set of breakthrough curves is developed and thereby the breakthrough times are obtained. The break-through concentration is taken as 0.1 mg/L as Cr⁺⁶, following the guideline of Central Pollution Control Board (CPCB), India. Although it laid down Cu⁺² discharge limit through wastewater as 3.0 mg/L, it was considered as 0.1 mg/L for reuse of water in rinsing bath either for chrome plating or in bronze plating purpose.

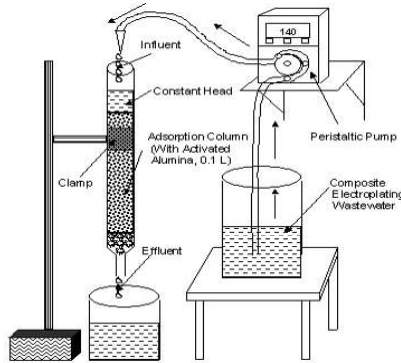


Fig. 2 Schematic arrangement of laboratory-scale Adsorption Column made of Activated Alumina (Grade AS 37)

IV. RESULTS AND DISCUSSION

A. Characterization

The results of characterization of Chrome and Bronze plating as well as composite wastewater are shown in Table-1. The characterization revealed that the wastewater contained heavy metals like Chromium and Copper. The value of Chemical Oxygen Demand (COD) is found to be low indicating low amount of oxidizable inorganic matter.

TABLE I RESULTS OF CHARACTERIZATION OF CHROME PLATING, BRONZE PLATING AND COMPOSITE WASTEWATER

Sl. No.	Source	Concentration of Parameters					
		pH	COD	Total Chromium	Copper	TDS	Iron
1.	Chrome Plating Bath	6.78-6.86	24.0-24.8	8.6-24.8	-	960-980	0.20
2.	Bronze Plating Bath	7.19-7.68	0.0	-	5.0 - 6.5	1300 - 1330	0.13
3.	Composite Wastewater	7.33-7.55	12.0-12.4	6.82-13.6	2.36 - 3.34	1040-1080	0.20

Note: All the parameters are expressed in mg/L except pH

B. Batch adsorption study

The effluent Chromium and Copper concentrations were analyzed by centrifugation of the sample and plotted in Figure 3 and Figure 4 respectively. The concentration profile of Chromium and Copper revealed that the removal was greatly affected by the dosage, but it was not significant

beyond a dosage of 50 g/L. Although, the Copper concentration attained its desirable value at a dosage of 50 g/L, the Chromium concentration was yet to be 0.1 mg/L. Also the difference between the equilibrium Chromium concentration for 50 and 60 g/L of Activated Alumina was nominal (particularly for a contact period of 60 Min.). Therefore, a dosage of 50 g/L of Activated Alumina was taken for further kinetic study.

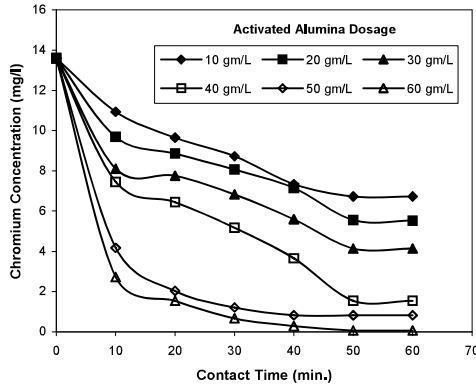


Fig. 3 Concentration of chromium at different dosages of Activated Alumina (0.3-0.6 mm) and contact period

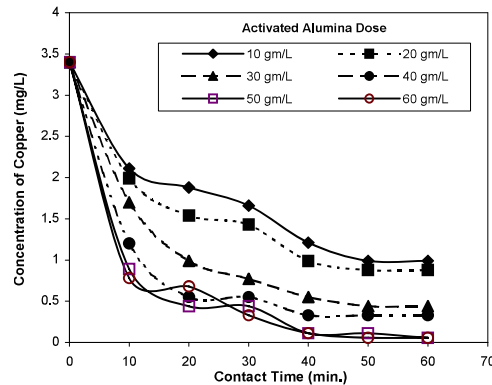


Fig. 4 Concentration of copper at different dosages of Activated Alumina (0.3-0.6 mm) at pH = 7.33

The percent removal of Chromium and Copper were evaluated with respect to the initial concentration as shown in Figure 5. It revealed that the percent removal of both Chromium and Copper increased rapidly up to a contact period of 15 Min. and almost ceased beyond this point. It was noted that this contact period for Chromium, i.e. time corresponding to the equilibrium concentration was less than that of the Copper. Therefore, the media was exhausted with chromium at a higher rate than Copper. Although, an

intersection of the removal curves of Chromium and Copper was observed, the most rational contact period for attaining equilibrium concentration was recognized as 45 Min. because it ensured more than 90 % of Chromium and Copper removal.

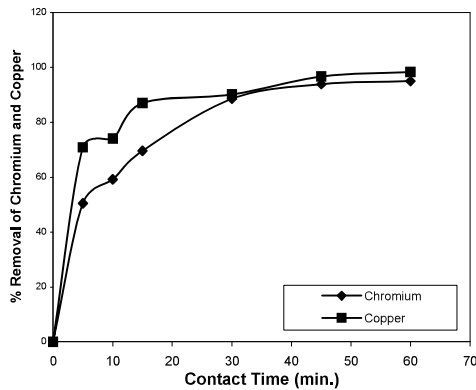


Fig. 5 Percent Removal of chromium and copper by adsorption on Activated Alumina from Composite Wastewater

C. Isotherm study

The result of analyses is presented in Table-2, which are used for development of different Isotherms.

Sl. No.	Adsorbent Dosage (gm/L)	Chromium Concentration (mg/L)	Copper Concentration (mg/L)
1.	10	4.17	0.89
2.	20	2.04	0.44
3.	30	1.21	0.44
4.	40	0.83	0.11
5.	50	0.81	0.11
6.	60	0.81	0.055

(Note : The contact period is 45 Min. and Volume of sample is 100 ml)

Firstly, the values of equilibrium concentration of chromium as well as the mass of the activated alumina were used to fit with the Langmuir's Isotherm. The relationship [3] has been developed with the following linear equation and a correlation coefficient (R²) value of 0.9838 is obtained. The equation of best-fit line is found as Y = 3.0977 X + 0.1702, where the slope and intercept are calculated as, X_m = 5.8754 and b = 0.0549.

$$\frac{1}{X} = \frac{1}{X_m} + \frac{1}{C_e} \left[\frac{1}{b \cdot X_m} \right] \quad (1)$$

In order to develop the Freundlich Isotherm for chromium removal, the observed values of log (x/m) and corresponding log C_e are fitted in the following expression. of Freundlich [20]. The relationship is obtained as y = 0.7915 x - 0.4935 having R² value of 0.958 and the constants are determined as K = 0.3210 and n = 1.2634.

$$\log \left[\frac{X}{M} \right] = \log K + \frac{1}{n} \log C_e \quad (2)$$

To develop the BET Isotherm [3], the data have been arranged in accordance with the respective Isotherm equation as follows. The correlation of BET Isotherm yielded a straight line with a R² value of 0.9477. The values of constants are calculated from the equation of Best-fit, i.e. Y = 0.8893.X + 0.1883 as b = 5.7227 and X_m = 0.928.

$$\frac{C_e}{X \cdot (C_s - C_e)} = \frac{1}{X_m \cdot b} + \frac{(b - 1) \cdot C_e}{X_m \cdot b \cdot C_s} \quad (3)$$

Where, X = x/m, the amount of solute adsorbed, per unit weight of adsorbent m;
C_e = equilibrium concentration of solute;
C_s = solubility of solute in water at a specified temperature;
X_m = amount of solute adsorbed per unit weight of adsorbent required for monolayer adsorption;
and, b = a constant related to the heat of adsorption.

Similar isotherms have been plotted for adsorption of copper on activated alumina. The Langmuir isotherm for adsorption of copper on activated alumina has been developed with a relationship y = 0.7373x + 6.1328 and R² value of 0.825. The values of the constants are calculated as, X_m = 0.1630 and b = 8.20.

The Freundlich Isotherm for copper removal is generated with a relationship y = 0.4997 x - 0.6754 and R² value 0.9057. The values of the constants are calculated as, K = 0.2111 and n = 2.0012.

The BET isotherm for copper removal is also developed with a relationship y = 4.8181.x + 0.3128 and R² value of 0.9724. The constant parameters are determined as, b = 16.3993 and X_m = 0.1949.

The most appropriate kinetics for adsorption of chromium and copper on activated alumina has been selected by comparing R² values in different Isotherm correlations. Therefore, R² values for Langmuir, Freundlich and BET Isotherms in case of chromium and copper are compared as shown in Table 3.

TABLE III VALUES OF CORRELATION COEFFICIENT (R²) IN VARIOUS ISOTHERMS

Isotherm	Values of R ²	
	Chromium	Copper
Langmuir	0.9838	0.8250
Freundlich	0.9580	0.9057
BET	0.9477	0.9724

It is evident from Table 3 that, Langmuir and BET Isotherms are most appropriate to express the kinetics of removal of chromium and copper respectively. The respective best-fit Isotherms for chromium and copper are shown in Figure 6 and Figure 7 respectively. As R^2 value in case of chromium is more than 0.95 it can be concluded that there might be a heterogeneous surface offered by activated alumina during adsorption of chromium. The Isotherm for copper adsorption on activated alumina does not exhibit the monolayer nature. Moreover, the value of $1/n$ less than 1 indicates that the adsorption capacity gets reduced at the lower equilibrium concentrations.

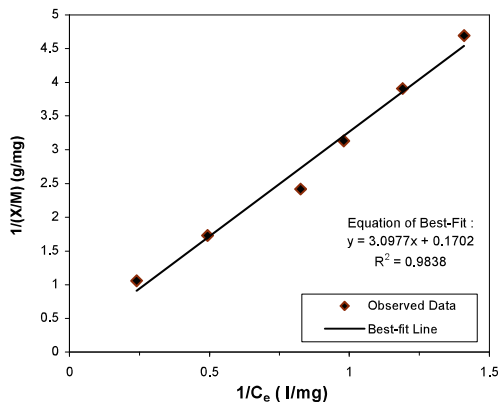


Fig. 6 Langmuir Isotherm for adsorption of chromium on Activated Alumina

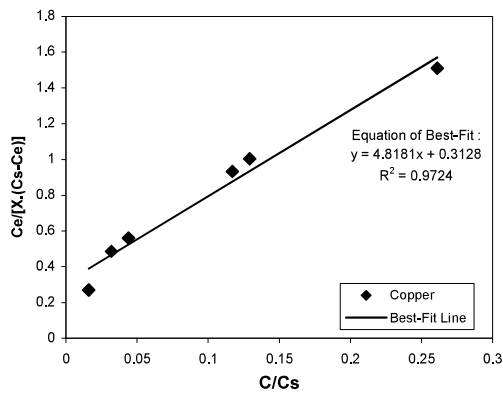


Fig. 7 BET Isotherm for adsorption of copper on Activated Alumina

D. Shape of adsorption Isotherm

The shape of the adsorption isotherm provides qualitative information about adsorption process and the extent of the surface covered by the adsorbate. Brunauer classified adsorption into five basic shapes, which are typically

developed by plotting the adsorption capacity (x/m) with respect to the equilibrium concentration (C_e). Following this, the chromium adsorption capacity of activated alumina is plotted against the respective values of C_e as shown in Figure 8, which resembles to Type I - Brunauer curve [21]. It also demonstrates that chromium adsorption on activated alumina does not proceed beyond monomolecular layer.

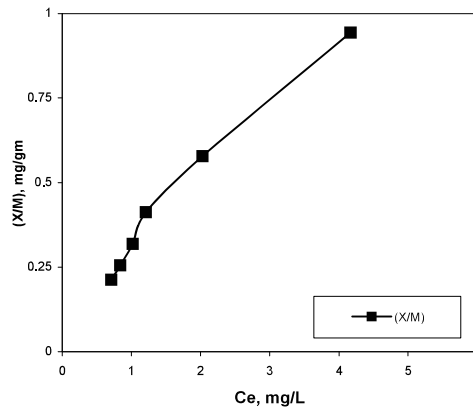


Fig. 8 Brunauer Isotherm for chromium adsorption on Activated Alumina

With a view to characterize the copper adsorption on activated alumina the values of (x/m) are plotted against C_e , as shown in Figure 9. It is observed that adsorption isotherm of copper satisfies Type IV - Brunauer Isotherm [21]. It depicts that surface of activated alumina is heterogeneous, not only in the surface structure but also in the distribution of surface energy. During the course of adsorption, the heat of adsorption did not remain constant for each incremental increase in adsorption.

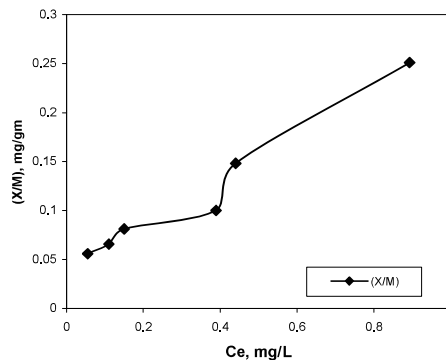


Fig. 9 Brunauer Isotherm for copper Adsorption on Activated Alumina

A steep initial drop of heat of adsorption with an increase of the material adsorbed indicates that the fast molecules arriving at the bare surface are preferentially adsorbed on the most attractive sites i.e. on the surface with minimum potential energy. As adsorption proceeds, the less active sites get occupied, which can be simulated as a case of multilayer adsorption.

E. Relative adsorption of Chromium and Copper by Activated Alumina

The efficiency of adsorption is directly proportional to the charge of ion and inversely proportional to the size of ion. It should be reflected in the relative adsorption of copper and chromium on Activated Alumina. Therefore, the percent removal of Chromium and Copper (from the Isotherm Study) are plotted along y and x-axis respectively as shown in Figure 10. The said graph depicts the percent removal of chromium expected for a specific percent removal of copper under the same condition. It is to observe that removal of chromium proceeds with a slow rate in comparison to the copper. It has also been observed that activated alumina could remove the colour almost completely from the composite wastewater.

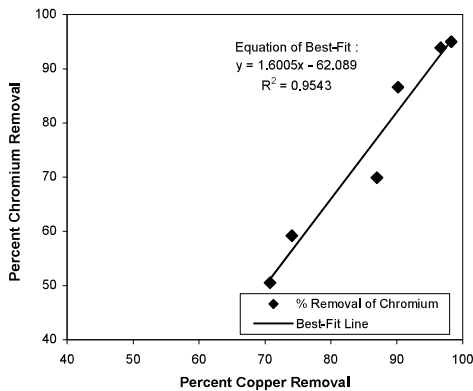


Fig. 10 Relative adsorption of copper in comparison to Chromium

F. Column study

The ratios of effluent to influent concentrations (C/C_0) of Chromium and Copper are plotted against time as shown in Figure 11 and Figure 12 respectively and the respective breakthrough periods are also found out. The breakthrough concentration is considered as 0.1 mg/L for both chromium and copper as mentioned earlier. The Breakthrough times are determined from the intersection of the Breakthrough curve and Breakthrough concentration line. The Breakthrough times for different column depths of 25, 35 and 50 cm for Chromium and Copper are shown in Table 4.

Although the concentration of copper is less than that of chromium, the Breakthrough time is observed to be higher in case of chromium. It may be attributed to the fact that the

activated alumina adsorbs chromium with a faster rate than the copper. It might be due to higher affinity of activated alumina to chromium than the copper. It is also supported by literature that ionic radius of CrO_4^{2-} (where Chromium is in Cr^{+6} form) is about 3.5 times that of Copper [21].

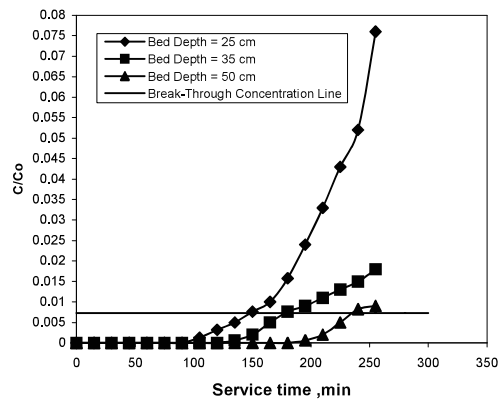


Fig.11 Breakthrough curves for chromium on Activated Alumina columns with Composite Wastewater

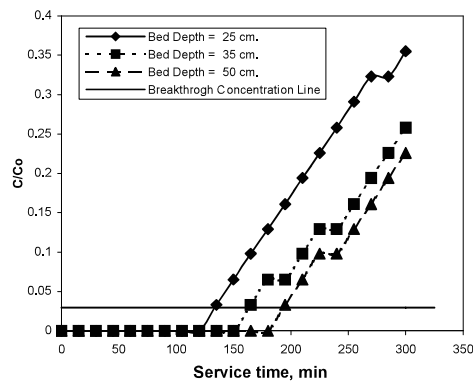


Fig. 12 Breakthrough curves for Copper on Activated Alumina columns with composite wastewater

TABLE IV BREAKTHROUGH TIMES FOR CHROMIUM AND COPPER USING COMPOSITE WASTEWATER

Bed Depth (cm)	Breakthrough Time (Min)	
	Chromium	Copper
25	150 min	135 min
35	180 min	165 min
50	235 min	195 min

During the column study chromium concentration in the effluent was traced earlier than the copper for all the cases, which indicates the more service period for the copper removal. While Breakthrough time is considered for any element, it must be checked whether the concentration of the other element remains within the desirable limit. In the present study, the Breakthrough time for chromium (from Figure 11) can be used in Figure 12 to determine the respective effluent concentration of copper. Consequently, the (C/C_0) values are obtained for 25, 35 and 50 cm depth of the column as 0.065, 0.065 and 0.098 giving copper concentrations of 0.221, 0.221 and 0.333 mg/L respectively, which are appreciably lower than the permissible value of 3.0 mg/L. In the present case the breakthrough times are determined corresponding to a hydraulic loading rate of $1.69 \text{ m}^3/\text{m}^2/\text{h}$.

G. Process design of Adsorption Column by Bohart-Adams Model

The Bed Depth-Service Time (BDST) method as proposed by Bohart and Adams has been used for designing the Activated Alumina Column [3] for the removal of chromium and copper from the real wastewater. To develop the BDST relationship the data obtained from three columns are plotted with Breakthrough time as Service time along abscissa and the column depth along ordinate. Two linear graphs are obtained for chromium and copper as shown in Figure 13 and Figure 14 respectively corresponding to three column depths. The BDST curve for chromium is represented by the equation, $y = 3.4211 \cdot x + 62.895$ with R^2 value of 0.9972, whereas BDST curve for copper is expressed by the equation, $y = 2.3684 \cdot x + 78.158$ with R^2 value of 0.9868.

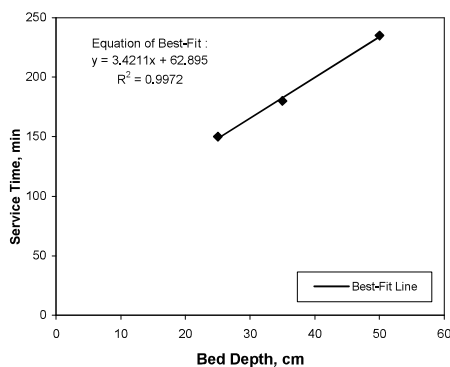


Fig. 13 Bed Depth Service Time (BDST) curve for chromium on Activated Alumina

The usual concentration of chromium and copper in composite wastewater in an identical electroplating plant is observed as 90 to 100 mg/L and 8 to 10 mg/L respectively. For the sake of design of a suitable Adsorption column for simultaneous removal of chromium and copper, their respective concentrations in real wastewater are considered as

100 mg/L and 10 mg/L. It is to simulate the fact that the physico-chemical treatment is undertaken only when the wastewater in the storage tank almost attains the above-mentioned concentration of chromium and copper.

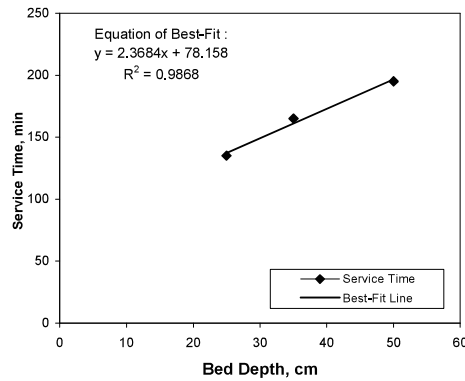


Fig. 14 Bed Depth Service Time (BDST) curve for Copper on Activated Alumina

The necessary calculation for designing the adsorption column is shown hereunder.

The BDST relationship for Chromium gives

$$\text{Service Time in min.} = 3.4211(\text{Bed Depth in cm.}) + 62.895 \quad (4)$$

Whereas, The BDST relationship for Copper is

$$\text{Service Time in min.} = 2.3684(\text{Bed Depth in cm.}) + 78.158 \quad (5)$$

The wastewater volume is observed as 8000 litres in a month as a single discharge. On a higher side it may be considered that the wastewater is discharged @ $1 \text{ m}^3/\text{day}$ for one 8 hours working period and this is to be treated and recharged again in the rinsing bath. The activated alumina column having a diameter of 500 mm is firstly considered for which the changed hydraulic loading rate would be $0.51 \text{ m}^3/\text{m}^2/\text{h}$.

As a result, the change in the flow rate will cause a change in slope.

$$\begin{aligned} a' (\text{New Slope}) &= \frac{V}{V'} * a (\text{old slope}) \\ &= \frac{1.69}{0.51} * 3.4211 = 11.33 \end{aligned}$$

Also, the changed feed concentration for designing the adsorption column can be expressed as

$$a'' = \frac{C_0}{C_1} * a'$$

a'' can be considered as the new slope due to new feed concentration, where C_0 and C_1 are the old and new feed concentrations respectively and a' is the slope obtained with changed loading rate. Therefore, for a Chromium concentration of 100 mg/L in the feed waste stream

$$a'' = \frac{13.6}{100} * 11.33 = 1.54$$

As a result of change in the feed concentration there will be a change in the intercept, which is calculated as

$$b' = b \frac{\ln \frac{C_1}{C_F}}{\ln \frac{C_0}{C_B}}$$

$$= 62.895 \frac{\ln \frac{100}{0.1}}{\ln \frac{13.6}{0.1}}$$

$$= 11.97$$

Therefore, the new equation correlating service time and bed depth for a continuous 8 hrs of operation will be

$$\text{Service time in min.} = 1.54 * (\text{Bed Depth in cm.}) + 11.97$$

$$8 \times 60 = 1.54 * (\text{Bed Depth in cm.}) + 11.97$$

$$\text{Bed Depth} = (480 - 11.97) / 1.54 = 304 \text{ cm.}$$

Similarly, the bed depth is also evaluated for new applied concentration of copper with a changed flow rate i.e. $0.51 \text{ m}^3/\text{m}^2/\text{h}$ as 167 cm. , which is lower than that required for chromium. Therefore, the Adsorption column having diameter 500 mm requires bed depth of 304 cm. , which is capable to adsorb both chromium and copper concentration up to 0.1 mg/L in both cases. However, regeneration of the bed would be required after every 8 hours operation period.

H. Conclusions

The present study reveals that the batch discharge from Chrome and Bronze Plating unit can be treated by adsorption in Activated Alumina, when two waste streams are mixed together as a composite waste sample. However, prior to go for adsorption process, chemical treatment of bronze plating waste stream for cyanide destruction is essential to prevent toxic hazard. Activated Alumina (Grade AS 37) shows a good performance at existing pH for substantial removal of chromium and copper from the composite wastewater (prepared with chrome and bronze plating wastewater in 1 : 1 ratio) within a short contact time. The adsorption kinetics follows mostly Langmuir Isotherm for chromium and in case of copper, BET Isotherm appears to be best. With regard to simultaneous removal of chromium and copper, Activated Alumina provides a considerable breakthrough time at different column depths. The adsorption kinetics for chromium and copper is influenced by each other and therefore it may necessarily not be used for the synthetic solution of copper and chromium independently.

The Bed Depth Service Time (BDST) relationship, developed from continuous operation in the column study shows a good correlation co-efficient (near about 99%) and it

can be successfully utilized for prediction of bed depth for a given influent concentration and hydraulic loading rate. According to the present practice of discharge and subsequent chemical treatment, an adsorption column of Activated Alumina (AS 37 Grade, $0.3 - 0.6 \text{ mm}$ size) is designed for a chromium and copper concentration of 100 mg/L and 10 mg/L respectively and a flow rate of $1 \text{ m}^3/\text{day}$, using the BDST relationship. The dimension of the proposed adsorption column (Diameter 500 mm and height 304 cm) provides a viable solution towards the replacement of existing chemical treatment method.

ACKNOWLEDGMENT

The authors express their sincere thanks to M/s Jessop & Co. Ltd., Kolkata for extending co-operation in the waste survey and the collection of wastewater samples.

REFERENCES

- [1] R. Sarkar., *General and Inorganic Chemistry Part I and Part II*, New Central Book Agency (Pvt.) Ltd., Kolkata, 1984.
- [2] P. K. Goel, *Water pollution, causes, effects and control*. New Age International (P) Limited, New Delhi, 1997.
- [3] S. D. Faust and O. M. Aly., *Adsorption processes for water treatment*. Butterworth Publishers, Stoneham, 1987.
- [4] D. P. Tewari, K. Promod, A. K. Mishra, R. P. Sinha and R. P. S. Shrivastav, "Removal of toxic metals from electroplating industries (effect of pH on removal by adsorption)," *Indian Journal of Environmental Health*, vol. 31, no. 2, pp. 120-124, 1989.
- [5] N. Shukla and J. K. Moitra, "Adsorption studies of copper in wastewater using different treatment materials", *Journal of the Institution of Public Health Engineers, India*, vol. 3, Jul-Sept, pp. 52-54, 1994.
- [6] A., Kapoor and T. Viraraghavan, "Use of immobilized bentonite in removal of heavy metals from wastewater", *Journal of Environmental Engineering*, vol. 124, no. 10, October, pp. 1020-1023, 1998.
- [7] M. Prasad, S. Saxena, S. S. Amritphale and N. Chandra, "Evaluation of aqueous copper removal by adsorption on low grade phosphate mineral surface", *J. Institution of Chemical Engineers, Section A*, vol. 42, no. 3, July-Sept, pp. 163-169, 2000.
- [8] A. K. Samanta, J. K. Basu and G. Kundu, "Removal of hexavalent chromium from aqueous solution by using low-cost adsorbent", *Indian J. Environmental Protection*, vol. 20, no. 10, October, pp. 754-760, 2000.
- [9] M. J. Kapadia, R. P. Farasram, D. H. Desai and M. M. Bhatt, "Removal of copper from effluent by fly ash", *Indian J. Environmental Protection*, vol. 20, no. 7, July, pp. 521-527, 2000.
- [10] R. Schmuhl, H. M. Kreig, and K. Keizer, "Adsorption of Cu(II) and Cr(VI) ions by chitosan : kinetics and equilibrium studies", *Water SA*, vol. 27, no. 1, January, pp. 1-7, 2001.
- [11] S. Yu, Z. L. He, C. Y. Huang, G. C. Chen and D. V. Calvert, "Adsorption-desorption behavior of copper at contaminated levels in red soils from China", *Journal of Environmental Quality*, vol. 31, pp. 1129-1136, 2002.
- [12] M. M. Aslam, I. Hassan, M. Malik, and A. Matin, "Removal of copper from industrial effluent by adsorption with economic viable material". *Electronic Journal of Environmental, Agricultural and Food Chemistry*, vol. 3 no. 2, pp. 658-664, 2004.
- [13] Manuel Algarra, Victoria M. Jiménez, Enrique Rodríguez-Castellón, Antonio Jiménez-López and José Jiménez-Jiménez, "Heavy metals removal from electroplating wastewater by aminopropyl-Si MCM-41", *Chemosphere*, vol. 59, pp. 779 - 786, 2005.
- [14] Suwannee Junyapoon and Suttawadee Weerapong, "Removal of hexavalent chromium from aqueous solutions by scrap iron filings", *KMITL Science and Technology Journal*, vol. 6, Jan-Jun, pp. 1-12, 2006. Available at <http://www.kmitl.ac.th/ejkmmitl/vol6no1/content.htm>.
- [15] E. Álvarez-Ayuso, A. García-Sánchez and X. Querol, "Adsorption of Cr(VI) from synthetic solutions and electroplating wastewaters on

- amorphous aluminium oxide", *Journal of Hazardous Materials*, vol. 142, no. 2, April, pp. 191 – 198, 2007.
- [16] Shiao-Shing Chen, Chih-Yu Cheng, Chi-Wang Li, Pao-Hsuan Chai and Yu-Min Chang, "Reduction of chromate from electroplating wastewater from pH 1 to 2 using fluidized zero valent iron process", *Journal of Hazardous Materials*, vol. 142, no.2, April, pp. 362 –367, 2007.
- [17] <http://www.cpcb.nic.in/Environmental%20Standards/Effluent/standard26.html>.
- [18] American Public Health Association, American Water Works Association and Water Pollution Control Federation, U.S.A., *Standard Methods for the Examination of Water and Wastewater*, 16th Edition, 1985.
- [19] B. D. Jeffery, J. Bassett, J. Mendham and R. C. Denney, *Vogel's Text Book of Quantitative Chemical Analysis*, 5th Edition, Longman Scientific and Technical Publishers, New York, 1989.
- [20] Metcalf and Eddy Inc., *Wastewater Engineering, Treatment, Disposal and Reuse*. Tata McGraw Hill, 3rd Edition, New Delhi, 1991.
- [21] Rakshit P.C., *Physical Chemistry*, Sarat Book House, Kolkata, 1969.

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Annex 5: Confidential overview of all approved tests of PVD coatings for PoPAA



Type of test	Property	Test	Home-made	Results	Ref.nr.
ADHESION	Cross Hatch test			Pass	1
	Saw Grind 22 tooth/inch 16-18 tooth/inch			Pass	2
ABRASION	Crock meter			Pass	3
	Rub Abrasive Test			Pass	4
	Taber Abrasion			Pass	5
	Taber Abrasion			Pass	6
	Resistance to gritting			Pass	7
	Scratch resistance under load			Pass	8
	Thumbnail Hardness			Pass	9
	CHIP RESISTANCE	Gravelometer			Pass
Gravelometer				Pass	11
CORROSION	Cass test			Pass	12
	Cass test			Pass	13
	Salt Spray Test			Pass	14
	Cass Test			Pass	15
	Corrosion resistance			Pass	16
	Climate test			Pass	17
	"Russian" Mud Test			Pass	18
	WEATHERING TEST (partly overlapping with corrosion)	Environmental cycle test			Pass
Environmental cycle test				Pass	20
Environmental Cycle Test				Pass	21
Environmental Cycle Test				Pass	22
Thermal cycle test				Pass	23
Thermal cycle test				Pass	24
Resistance to corrosion (gritting+ thermal+ corrosion)				Pass	25
Resistance to thermal shock and corrosion (thermal+ corrosion)				Pass	26
WATER RESISTANCE	humidity test + adhesion/ gravelometer			Pass	27
	Humidity test			Pass	28
	Resistance to water immersion			Pass	29
TEMPERATURE RESISTANCE	Hot water resistance			Pass	30
	Temperature resistance			Pass	31
AGING RESISTANCE	Aging resistance			Pass	32
	Temperature resistance			Pass	33
	Hydrolysis Aging			Pass	34
	QUV-B 1000h			Pass	35
	QUV-2000h			Pass	36
FLUID AGENTS RESISTANCE	Resistance to cleaning agents and synthetic sweat			Pass	37
	Resistance to cleaning agents and synthetic sweat			Pass	38
	resistance to occasional fluid contacts			Pass	39
	Resistance to high pressure			Pass	40
	Resistance to Sodium Hydroxide			Pass	41
	Resistance to Volatile Oil			Pass	42
	Resistance to regular gasoline			Pass	43
	Resistance to gasohol (E10)			Pass	44
	Resistance to Oxynol (MT5)			Pass	45
Resistance to H2SO4			Pass	46	



Annex 6: APP presentation on PVD market and market developments



Vacuum Coating Machines

MARKET FOR COATINGS ON PLASTIC PRODUCTS
FOR DECORATIVE AND AUTOMOTIVE PARTS

INTRODUCTION

1. Availability of Market data
2. Calculation of productivity
3. Capacity for Scenario 1
4. Capacity for Scenario 2
5. Conclusions

AVAILABILITY OF MARKET DATA

For the Alliance of PVD Providers (APP) it has been extremely difficult to find reliable data for the estimation of the European market for PoPAA:

- The number of applications using PVD is still limited, as the technology is new in the application field.
- The market data from the electroplaters are kept confidential throughout the Application for authorisation (AfA) of Gerhardi (consultation number 0071-01).

Sources for market data lead us to work with two scenarios:

1. From the Analysis of Alternatives in the Gerhardi AfA it can be distilled that the European market for PoPAA is around 14 Mio. m² in 2016
2. The APP has obtained the report "Plating on Plastics (PoP) Market Size and Industry Analysis, 2016-2023" of Global Marketing Insights, Inc. Page 152 gives an overview of the European PoPAA market.

Needless to say, APP would really like to be able to work on the basis of the market data used in the AfA and invites the applicants to disclose those!

AVAILABILITY OF MARKET DATA

SCENARIO 1 (based on conservative estimate of the sum of different pieces of available data in the AfA):

- Data based upon conservative estimate of market size: 14 million m²
- The APP has put in its best efforts derive this estimate from different pieces of information in AfA added up together.
- Same market growth is applied as for scenario 2: 6% per year.

Year	POP capacity- automotive for Europe in Mio.m ²	CAGR
2016	14,0	6,00%
2017	14,8	6,00%
2018	15,7	6,00%
2019	16,7	6,00%
2020	17,7	6,00%
2021	18,7	6,00%
2022	19,9	6,00%
2023	21,1	6,00%
2024	22,3	6,00%
2025	23,7	6,00%
2026	25,1	6,00%
2027	26,6	6,00%

AVAILABILITY OF MARKET DATA

SCENARIO 2 (based on third party market report):

- The APP has obtained the report “**Plating on Plastics (PoP) Market Size and Industry Analysis, 2016-2023**” of **Global Marketing Insights, Inc.**
- Page 152 gives an overview of the European PoPAA market:

TABLE 170 Europe POP volume estimates by application, 2016 - 2023, (Million Square Meter)

Application	2016	2017	2018	2019	2020	2021	2022	2023	CAGR (2016-23)
Automotive	26.9	28.4	30.1	31.9	33.8	35.9	38.1	40.5	6.0%
Domestic fittings	3.3	3.5	3.7	3.9	4.1	4.4	4.6	4.9	5.8%
Electrical & electronics	2.4	2.5	2.6	2.8	2.9	3.0	3.2	3.4	5.1%
Others	1.6	1.7	1.8	2.0	2.1	2.2	2.4	2.5	6.5%
Total	34.2	36.1	38.2	40.5	42.9	45.5	48.3	51.3	6.0%

Source: NMFRC, ASTM, REACH, U.S. EPA, OICA, Plastics Decorative Magazine, Primary Interviews, Global Market Insights

AVAILABILITY OF MARKET DATA

MARKETING DATA SCENARIO 2:

- The report predicts a growth rate of the market of 6% (CAGR) for PoPAA.
- This results in an estimate of overall market demand for PoPAA of a total of:
 - **42.900.000 m2 in 2024.**

Year	Calculated Growth	POP capacity-automotive for Europe in Mio.m ²	CAGR
2012		21,6	
2013	5,56%	22,8	
2014	5,70%	24,1	
2015	5,39%	25,4	
2016		26,9	6,00%
2017		28,5	6,00%
2018		30,3	6,00%
2019		32,1	6,00%
2020		34,0	6,00%
2021		36,0	6,00%
2022		38,2	6,00%
2023		40,5	6,00%
2024		42,9	6,00%
2025		45,5	6,00%
2026		48,2	6,00%
2027		51,1	6,00%

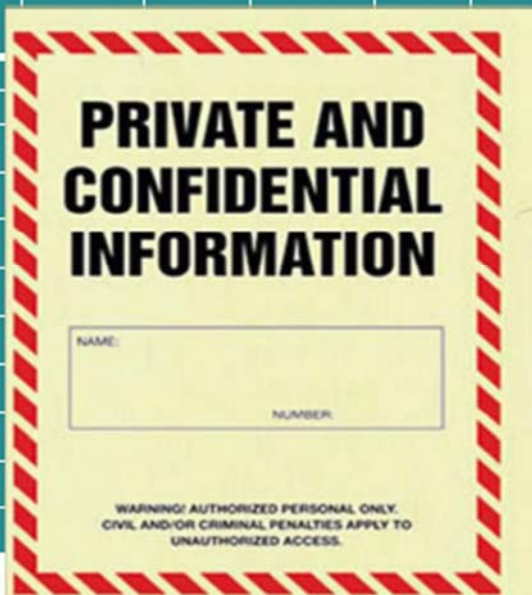
CALCULATION OF PRODUCTIVITY

Data for calculation:

- The system runs for 50 weeks and is weekly for 8 hours under maintenance.
- The calculated scrap rate is 15% (as usual for lacquer lines).
- The yearly production is taken as the average for flat and three-dimensional products.

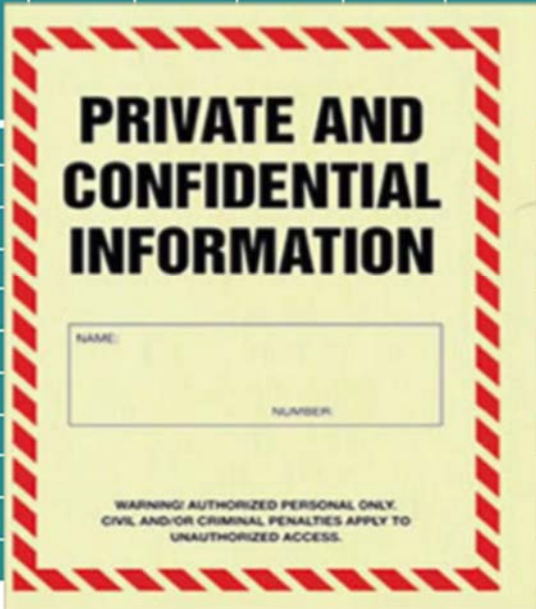
CAPACITY FOR SCENARIO 1 +7 YEARS

YEAR	Ionbond	Hauzer	Oerlikon	Kolzer	VTI	Total capacity	APP	Total Demand	APP share of total demand
2016						1,44	14,0	10,29	
2017						2	14,8	13,51	
2018						2,2	15,7	14,01	
2019						3,3	16,7	19,76	
2020						6,2	17,7	35,03	
2021						10,6	18,7	56,68	
2022						17,3	19,9	86,93	
2023						25,4	21,1	120,38	
2024						34,5	22,3	154,71	
2025						44,2	23,7	186,50	
2026						54,8	25,1	193,23	



CAPACITY FOR SCENARIO 2 +7 YEARS

YEAR	Ionbond	Hauzer	Oerlikon	Kolzer	VTI	Total APP capacity	Total Demand	APP share of total demand
2016						1,44	26,9	5,35
2017						2	28,5	7,02
2018						2,2	30,3	7,26
2019						3,3	32,0	10,31
2020						6,2	34,0	18,24
2021						10,6	36,0	29,44
2022						17,3	38,2	45,29
2023						25,4	40,5	62,72
2024						34,5	43,0	80,23
2025						44,2	45,5	97,14
2026						54,8	48,2	113,92



CONCLUSIONS

- Alternative technologies based upon lacquer + PVD are fulfilling technical requirements as expected by the automotive industry.
- Several matured technologies are available and already producing in series for the automotive industry.
- Different scenario's for future market demand for PoPAA can be covered by PVD technology.

WE ARE AT YOUR COMPLETE DISPOSAL.
THANK YOU!

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