Analysis of infrared optical polishing effluents and reduction of COD and TSS levels by Ultrafiltration and Coagulation/Flocculation

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Abstract

Samples of polishing effluent produced during infrared optics manufacture were analyzed. Their particle size, composition, Zeta potential, Chemical Oxygen Demand (COD), Total Suspended Solids (TSS) and Settable Solids (SetSol) were determined. Feasibility of ultra-filtration and coagulation/flocculation were investigated as treatment methods to reduce both COD and TSS. It was found that effluents consisted of a suspension of micro and nano particles. Effluent particle size distribution reflected the removal rate of the originating polishing process. Their composition was primarily germanium and other polished substrates as well as polishing abrasives. The effluent Zeta potential was highly negative and prevented particle settling. COD of all specimens was very high; which prevented sewage discharge. Laboratory scale trials using Ultra-Filtration (UF) showed substantial COD abatement of up to 74.1%. TSS was reduced to zero after UF. Comparable coagulation/flocculation COD abatement was demonstrated for the highest COD sample.

Keywords: Polishing effluents, industrial, wastewater treatment, analysis, industry, effluent

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1 Introduction

High value optics manufacture is an established industry in the UK. A wide range of scientific and technological worldwide industries such as medical, defense and aerospace rely on these precise elements.

Manufacture of high value optics relies heavily on polishing processes. Conventional polishing employs slurries containing abrasive particles that flow between the surface being polished and a pad. The slurry may have a specific pH to generate a slight etching of the surface that in combination with the suspended abrasives removes material from the substrate [1]. Polishing of optical components usually employs a series of progressively finer abrasive media to grind away the higher points of a surface profile until this becomes "smooth". The different polishing stages can be generally classed by the abrasive size employed. For example, larger abrasive particles, of typical average of up to 45 μm, are used for rapid stock removal. Subsequent lapping operations may employ "mid-range" abrasive sizes ranging from 14 to 6 μm. Final polishing is typically achieved using abrasives ranging from 4.5 μm to submicron. Common slurry abrasives include diamond, silicon carbide, alumina and silica. Polishing slurries can be both oil, soluble or emulsions.

Although polishing slurries can be re-circulated and are commonly reused, there is a critical point where their abrasive concentration falls below optimum. At this point, polishing efficiency is severely affected [2]. Consequently, these "worn" slurries are disposed and a "fresh" batch is prepared. Due to the industry growth [3] and diversification [4, 5] effluent volume from optical polishing is increasing and it needs to be disposed responsibly.

41 This study focuses on the polishing effluent generated by the Infra-red (IR) optical industry. This

42 forms a substantial portion of the UK high value optics industry. The substrate materials

43 typically polished are germanium, silicon, gallium arsenide, zinc selenide, zinc sulphide, glasses

44 and other miscellaneous IR materials. Night vision systems are the most common applications of

45 these materials. Approximately 10,000 liters of wastewater are generated per year at this

46 facility by 10 dedicated machines included in this study.

47 Currently, there are a large number of publications related to disposal management of chemical

48 mechanical polishing (CMP) effluents from the semiconductor industry. Effluent disposal in the

49 photovoltaic industry has also registered a growing interest [6-9] . However, literature relating

50 to the physical or chemical properties, composition and disposal of IR polishing effluents is still

51 scarce. In this work, we set to determine the composition, particle size distribution, SetSol, COD,

52 TSS and Zeta potential of optical IR polishing effluents from "worn" slurry samples collected

53 from a major European facility. To simplify this analysis, the scope of the research has been on

54 reduction of COD and TSS within local sewage regulations. Ultra-filtration and

55 coagulation/flocculation have been initially investigated as routes to achieve this. In England

56 and Wales, sewage effluent disposal must conform to the water industry act 1991 [10]. Local

57 consent limits issued for these effluents are of 1000 and 500 mg/l for COD and TSS, respectively.

58 Other elements detailed in the consent are copper, zinc, cadmium, lead, chromium and iron. All

59 of these are limited to 2mg/l.

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2 Experimental

64 6 different waste slurry samples, A to F, were collected from a large UK Infrared specialist

65 optical polishing facility. The samples were collected at the end of 6 different production lines.

66 These polishing processes ranged from rapid material removal to final polishing for a range of

67 different substrate materials. Table 1 illustrates some of the sample characteristics noted at an

68 initial visual assessment following their collection. Table 1 also gives the polishing processes

69 originating the samples and abrasive type used.

70 Characterization of the effluent composition, particle size distribution, COD, SetSol, TSS, and

71 Zeta potential enabled specification of feasible routes for treatment. Prior to characterization

72 each sample was thoroughly homogenized by shaking it for 30 seconds before a subsample was

73 taken. This procedure was determined by initial microscopy homogenization studies.

2.1 Particle size distribution and composition of polishing slurry effluents

76 Characterization of the slurry particle size distribution is critical for effective treating of polishing

77 slurries. This is even more important if treatment techniques such as ultra-filtration are to be

78 considered. In the present work, particle size distribution was performed using Dynamic Light

79 Scattering (DLS) techniques [11]. This was conducted in 2 stages to ensure best resolution.

80 Initially a Mastersizer 2000 (Malvern Instruments, Worcester, UK) was used to characterize the

81 sample solids down to 1μm. Median and quantiles were calculated. After this, the particle

82 distributions were further characterized using a Nanosizer (ZS Malvern Instruments, Worcester,

4

83 UK). Prior to this, the samples were filtered to remove all particles over 1 μm. Each sample was

84 characterized at least three times to ensure repeatability. In addition, optical and Scanning

85 Electron Microscopy (SEM) were used to complement the DLS characterization.

86 The slurry samples were also analyzed to accurately establish their chemical composition. This

87 was conducted using both Energy Dispersive Analyses (EDS) and X-Ray Diffraction (XRD). Slurry

88 dry-powder specimens were prepared. Typically, 140 ml subsamples of each of the slurries were

89 set in an oven at 105 ^{o}C until all fluid had evaporated leaving a dry powder. These analyses also

90 identified unexpected or hazardous residual elements that required special treatment.

91 2.2 Characterization of polishing effluent COD, SetSol, TSS and Zeta
92 Potential

93 COD is a measure of the amount of oxygen used in chemical oxidation of inorganic and organic

94 matter contained in wastewater. COD together with other wastewater parameters such as TSS,

95 is widely considered an indicator of pollution degree and environmental impact. In order to

96 comply with effluent discharge regulations, wastewater effluents often require treatment to

97 abate COD and TSS prior to sewer disposal.

98 COD values were calculated for all samples using a standard procedure [12] for the examination

99 of water and wastewater. For this, the test effluent is heated up to 148 °C for 2 h with

100 potassium dichromate ($K_2Cr_2O_7$) and concentrated sulphuric acid (H_2SO_4) in the presence of

101 silver (Ag) as catalyst. After cooling, the COD values were measured by photometry (NOVA 60 by

102 MERCK, Darmstadt, Germany). Results were expressed in mg/l.

103   Settleable solids (SetSol) were measured using an Imhoff cone in accordance with standard

104   procedures [13]. One liter of each of the samples after thoroughly mixing was allowed to settle.

105   After one hour, the volume of solids (ml) that settled at the cone apex was measured.

106   Following this procedure, the total suspended solids (TSS) was measured [14] 100 ml of each

107   effluent sample without settleable solids were filtered using a Buchner flask and paper filter

108   with particle retention of 1.2 µm (Whatman type GF/C glass-fiber, Leicester, UK). Following

109   filtration, the paper was dried at 105 ^{o}C in an oven for 2h. The net weight of the retained

110   particles was measured using an analytical balance to determine the TSS of each sample:

111   **Equation 1**

$$TSS = \frac{w_2 - w_1}{V}$$

112
113   *TSS*   total suspended solids in mg/l
114   *w2*   paper filter + dried suspended solids residual weight (mg)
115   *w1*   paper filter weight
116   *V*   volume of sample filtered (l)
117

118   Zeta potential is the electrical potential that exists at the shear plane of a particle. It describes

119   the electrostatic interactions of particles in a fluid and can be used as a measure of its

120   flocculation state. The Zeta potential was measured with a Zetasizer (Malvern Instruments,

121   Worcestershire, UK) at ambient temperature.

122   Each experiment was repeated at least twice for repeatability.

2.3 Ultra-filtration

From a manufacturing point of view, ultra-filtration (UF) provides a simplified approach and automation potential for efficient effluent disposal. Successful treatment of some semiconductor chemical-mechanical polishing effluents using UF and reverse osmosis (RO) [15] and UF preceded by chemical treatment have been previously reported [6]. UF trials were conducted at laboratory scale. The cross flow filtration pressurized (N_2) system removed micro and nano size particles using a porous membrane. Commercially available membranes (Polyethersulfone Biomax^{TM}, PB, MERCK, Darmstadt, Germany) with 67nm pore size were used. These membranes were chosen based on results from the previous particle size distribution measurement. The pressure was set to 0.7 atm. as specified by the membrane manufacturer. Polishing slurry subsamples of 350ml were filtrated. All experiments were conducted 3 times to verify repeatability. Following filtration, the COD of the samples was measured to analyze the effect of the filtration process.

2.4 Coagulation/flocculation

Coagulation/flocculation can be potentially a cost effective way of disposing IR polishing effluents. Coagulation/flocculation is the separation of fine suspended solids brought about using charge neutralization via a coagulant. Coagulation [16, 17] and more recently electrocoagulation [18-20] have been recently employed to investigate turbidity, total organic carbon (TOC) and COD abatement in semiconductor effluents. Similar techniques have been applied in the photovoltaic industry [7] .

143   The effectiveness of coagulation/flocculation was demonstrated for sample F. This was chosen

144   because of its high COD (6645 mg/l) and Z potential (-25.1 mV).

145   In order to ascertain the coagulation mechanisms of polishing effluents, initial titration tests

146   were conducted.   Ferric $Fe_2(SO_4)_3$ was used as the coagulant. $Fe_2(SO_4)_3$ is widely used in

147   wastewater treatment [21] and it was readily available to the researchers. Coagulation tests

148   were undertaken on a multi-jar tester. Samples of polishing slurry effluent were dosed with

149   varying amounts of $Fe_2(SO_4)_3$ relating to different Zeta potentials. Conditions involved rapid mix

150   at 300 rpm for 1 minute, a 15 min 30 rpm flocculation stage and a 15 min settlement period

151   [22].

3   Results and discussion

152

153   All polishing slurry samples typically had a cloudy appearance consistent with that of particles in

154   suspension. The samples color varied and this reflected particular components involved in each

155   of the polishing processes i.e. the substrate material, abrasive particles and solvents. The foam

156   reported on some of the slurry samples (see table 1) is attributable to aeration occurring during

157   slurry re-circulation in the polishing machine. Antifoams are commonly added to polishing

158   slurries to remedy excessive foaming that sometimes occurs. This was confirmed subsequently

159   for samples C, D and E at the optical factory shop. These antifoams may also contain oils.

160   However, a separate oily phase was not observed in any of these samples. Therefore it was

161   assumed that any oils were in emulsion.

3.1 Particle size distribution and composition

Figure 1 illustrates an example of the particle size distribution of a polishing effluent F. A narrow distribution around a mean of 1.15 µm is observed for this sample. This is consistent with the process origin of this sample being in lapping. This mean particle size is typical of a process with a very low rate of material removal. In general, the particle size distribution from each of the samples reflected the polishing process in which they were employed. Table 2 shows cumulative particle size distribution parameters. As seen, the median particle size for polishing effluent ranged from 100 to 1 µm approximately. The processes with greater rates of material removal yielded larger particle sizes and vice versa. Table 2 also illustrates the median and range of the submicron particle size distribution for all samples. For this measurement, the effluent mean particle size ranged from 460-180 nm. Figure 2 shows the submicron particle size distribution of sample F.

Figure 3 is a scanning electron microscope (SEM) image for sample D. A continuous layer of particulate ranging from 2 to 4µm can be observed. This correlates well with the particle size distribution previously obtained (Table 2).

Figure 4 shows a summary of the elements found in the EDS analysis conducted for each of the samples. A dominant presence of Germanium (Ge) was found. This was expected as Ge was the main substrate polished in most machines when the effluent samples were collected. Other substrates polished in the same machines included Silicon (Si), Zinc Selenide (ZnSe) and Zinc sulphide (ZnS) and these were also present in the analyses. Further elements found were related to the additives present in the polishing slurry. This was confirmed by their datasheets.

183   XRD analysis revealed the presence of GeO_2. This was confirmed by SEM microscopy. Figure 5

184   shows an image of GeO_2 nano-crystals found as precipitates in sample A. These were most likely

185   related to the abrasives used during the polishing process. Their approximate size is 500 nm.

186   Similar nano-crystals were also found on samples B and E.

187   In addition to the polished substrates, Carbon (C) and oxygen (O) were also present as chemical

188   species in all the results. Samples A and E showed small percentages of up to 4.21% of Zinc (Zn)

189   attributable to polished substrate residuals. Iron (Fe) was present in the analysis for sample C in

190   smaller amounts of up to 0.15%. This was not entirely unexpected. Metallic polishing-machine

191   tooling is often made of steel alloys.

192   In General, the EDS and XRD analysis did not return unexpected elements or compounds. These

193   analyses were clearly dominated by components relating to either to the polishing substrates or

194   the slurry abrasive used.

3.2 Polishing effluent COD, SetSol, TSS and Zeta Potential

196   Table 3 gives a summary of all effluents parameters calculated. The measured COD of all

197   samples as received ranged from 1789 to 6645 mg/l. This was much higher than the local

198   consent limit, currently set at 1000mg/l.

199   The measured TSS values of the samples A, E and F were compliant with the current discharge

200   consent limit at 500mg/l. samples B and C, showed TSS values that were close to this limit, while

201   that of sample D was many times over this limit at 4893 mg/l. These results correlated well with

202   the particle size distribution measurements previously conducted. The effluents whose

203   distribution overlapped the 1.2 μm filter pore size used, had a larger number of particles filtered

204   out and, a result a lower TSS. In contrast, sample D had a smaller submicron particle

205   distribution, and therefore a lower number of particles filtrated out. COD was re-measured

206   following the TSS procedure to observe the effect of filtration. Although a significant reduction

207   was observed for samples A and B, 54 and 55% respectively, the new COD values remained

208   greater than current local sewer discharge consent. The COD reduction observed in effluents A

209   and B was primarily due to their particle size distribution. These samples had the largest particle

210   sizes (see table 2), with a large number of these above the 1.2 μm filter pore size. In contrast for

211   samples C-F a lower COD reduction was observed. The polishing processes in which these

212   effluents originated are the finer removal stages in optical finishing. Therefore a large number

213   of particles in these effluents were in the nm range and meant they had a considerable

214   influence in determining the effluent COD. In view of these observations, it was confirmed that

215   ultra-filtration and coagulation/flocculation were viable treatment routes. Ultra-filtration

216   processes provide enhanced particle retention and an improved chance to abate COD and TSS

217   levels.

218   The very high negative Z potential values observed contributed to the low SetSol values

219   measured (Table 3). This was consistent with the initial visual assessment that reported that

220   almost or no precipitates observed. Therefore employing a settlement tank previous to effluent

221   treatment was not considered advantageous.

222   SEM sample dry preparation lead to the discovery of an oil phase in samples C, D and F. It was

223   subsequently confirmed that oil, antifoams and other additives had been used on these slurries.

224   As shown in Table 2 the samples with the higher COD had an oil phase. The effect of this oil

225   phase on the samples COD was investigated. Oils were extracted from the polishing effluents

226 and their concentration determined using the isolute SPE columns procedure [23]. After this,

227 COD was re-measured. The extraction procedure resulted in COD improvements of 11.1, 10.4

228 and 9.7 % for samples C, D and F, respectively. Oil concentration was estimated at 780 and 863

229 mg/l for samples C and F, respectively. A value for sample D could not be obtained, due to

230 column blockage.

231 **3.3 Ultra-filtration trials**

232 UF trials were conducted at laboratory scale using a N_2 pressurized cross flow filtration system.

233 In view of the particle size distribution obtained, a 64 nm pore size membrane was selected for

234 all effluents. This provided economical means of operation and sufficient level of filtration for

235 most particles. Figure 6 shows the COD values for each effluent sample before and after ultra-

236 filtration. As seen there is a significant improvement for all samples. Samples A, B, C, D and F

237 showed distinctive COD improvements ranging from 60 to 75%. Sample E, which had the lowest

238 COD at collection (1789 mg/l), observed a smaller but still favorable 34% abatement. Following

239 UF trials, samples A, B and E closely approached the current sewage discharge consent COD

240 limit at 1000 mg/l. We have attributed this to the substantial removal of solids after UF, including

241 some oxidizable, as shown in the EDS and XRD analyses. Further research is necessary establish its

242 fundamental mechanism.

243 Following UF, the samples appearance was clean and transparent. Due to the level of filtration

244 used, all particles larger than 1.2 μm were removed. Therefore the TSS for all samples after UF

245 was of 0 mg/l, within limits set for sewage discharge consent. This was expected. The results

246 were considered an experimental validation of compliance.

247   A similar treatment strategy was followed by Juang et.al [15] . Polishing effluents from the

248   semiconductor industry in Taiwan were treated by filtration first (1 µm), followed by UF (40nm).

249   Further reverse osmosis allowed the water permeate to meet tap industrial water reuse

250   standards. For photovoltaic effluents, Drouiche et al. [6] demonstrated feasibility of UF

251   preceded by chemical pretreatment for the regeneration of cutting fluids.

252   Laboratory trials have confirmed UF to be an effective method for treatment of IR effluent,

253   including samples found to have an oily phase (samples C, D and F). Permeation flux decline

254   caused by fouling and concentration-polarization effects of oils [24-26] and antifoams agents

255   [27] in metal working fluids have been previously reported. Clearly, these effects need to be

256   specifically investigated for IR effluents prior to widespread application of UF processes.

257   ## 3.4 Coagulation/Flocculation

258   Prior to coagulation/flocculation, titration experiments were conducted to investigate the

259   relation between the amount of coagulant solution (ferric $Fe_2(SO_4)_3$) and the resulting zeta

260   potential of sample F. Figure 7 shows the titration curve obtained. Zeta potential (mV) was

261   plotted in relation to the volume of $Fe_2(SO_4)_3$ solution (µl) used. It was observed that when the

262   coagulant solution volume exceeded 14 µl, larger positive Z potentials of over 10 mV were

263   obtained. Conversely, when less than 4 µl were used the Zeta potential was largely negative and

264   approached those of the initial sample measurements. Based on the observed behavior, a multi-

265   jar test was conducted. Four beakers were used with varying amounts of coagulant

266   corresponding to Z potentials of -10, -5, 0 and 5 mV. SetSol, TSS and COD were re-measured

267   after coagulation/flocculation. The jar test results are shown in table 6. As seen, when a Zeta

268 potential of +5mV was achieved, resulted in the highest SetSol, the lowest TSS and COD. This

269 was close to the optimum range of the Zeta potential previously observed between -11 and +3

270 mV using this coagulant for raw water [28] . Also, at +5 mV, the SetSol value improved from the

271 initial 0 to 367 ml/l, with a large amount of particles settling and the sample losing its

272 turbidness. The initial TSS value of sample F was already below legal discharge consent as

273 received (153mg/l), however, this was further reduced to 51 mg/l. In total, the COD was

274 reduced up to 68%, from 6645 to 1980 mg/l. A very similar reduction was previously obtained

275 using ultrafiltration, as shown in figure 6.

276 ## 3.5 Discussion summary

277 When compared, ultrafiltration and coagulation/flocculation, they both exhibit great potential

278 for treatment of polishing effluents from the IR industry. COD improvement was virtually the

279 same. Ultrafiltration achieved a further TSS reduction, virtually of 0 mg/l as opposed to the low

280 51 mg/l obtained with coagulation/flocculation. Nonetheless, this value is well under current

281 discharge consent at 500 mg/l.

282 Although the COD abatement was substantial, sewage discharge consent level was not achieved

283 by either of the techniques used during this initial work. Further studies should be conducted to

284 optimize both ultrafiltration and coagulation/flocculation parameters. For example, COD

285 improvement can be potentially achieved by further particle removal via reverse osmosis, as

286 previously demonstrated by Juang et. al [15]; or chemical pretreatment as demonstrated by

287 Drouiche et al. [6]. Small scale dilution can also be applied as a simple procedure for samples A,

288 B and E, since their UF COD was very close to the sewage disposal consent. COD of these will be

289 proportionally reduced to the water volume used for dilution. Evidently the main disadvantage

290 of this is the increase of the volume rate to discharge into the sewer. Nonetheless, The COD and

291 TSS improvements obtained using both UF and coagulation may potentially bring substantial

292 benefits to the environment while leading to cost effective polishing effluent disposal too.

293 Currently, disposal of these IR polishing effluents is mostly subcontracted and largely relies on

294 techniques such as high volume dilution.

295 IR optics manufacture involves a number of abrasive polishing processes and a range of

296 substrate materials. It has been found that these produce a range of effluents having different

297 composition, physical and chemical properties. As a result, characterization and disposal of the

298 IR effluents cannot be simply generalized.

299 Significant COD abatement has been achieved by the use of both ultrafiltration and

300 coagulation/flocculation. In terms of plant operational costs, ultrafiltration appears to incur the

301 highest costs compared with the simple tank process of electrocoagulation/flocculation. These

302 costs are associated with the supply of pressurized fluids, fouling, membrane replacement, etc.

303 [29]

304 It is clear from the present study that after use of UF and coagulation/flocculation there is no

305 need for large scale dilution, with reduction in the potential costs incurred and the volume of

306 effluents to be disposed.

4 CONCLUSIONS

307

308 1. Particle distribution in optical IR polishing effluents is made of a large number of particles

309   both in the micro and nano range. Measurements performed showed the particles size

310   ranged from a maximum of approximately 480 µm down to a few nm. The particle size

311   distribution was influenced by the polishing process removal rate in which the slurries were

312   used. Higher removal processes yielded larger particle sizes and vice versa.

313   2. The chemical composition of Optical IR polishing effluents is primarily dominated by the

314   polished substrate. Carbon and oxygen presence was also significant in the analyses. In

315   some of effluents, GeO_2 abrasive nano-crystals were found. Antifoam agents and other

316   polishing slurry additives used in some of the effluents produce residual oils. These had a

317   detrimental effect on their COD.

318   3. All samples as collected had high COD values that far exceed the local sewage disposal

319   consent. The effluent Z potential was highly negative for most samples. This influenced the

320   low settleable solids and the high turbidity observed.

321   4. Ultra-filtration is a powerful process for COD abatement in polishing slurries. For all

322   polishing slurries investigated, the COD was substantially reduced. Turbidity in post

323   ultrafiltration effluents was removed.

324   5. Coagulation/flocculation was demonstrated to be an effective process for COD reduction

325   and is comparable with ultra-filtration.

326   6. TSS were reduced to zero by the use of ultrafiltration. All particles larger than 1.2 µm were

327   filtered out.

Acknowledgements:

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table legends:

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409   **Table 1- Polishing effluent samples: Visual assessment at collection, process origin and abrasive type used**

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411   **Table 2- Particle size distribution by sample/process**

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413   **Table 3- COD, TSS, SetSol and Zeta potential results summary**

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415   **Table 4- sample F results after coagulation**

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Figure legends:

430   **Figure 1- Particle size distribution obtained using Malvern Mastersizer, sample F**

431   **Figure 2-Submicron particle size distribution, sample E**

432   **Figure 3-SEM image for sample D showing effluent particulates**

433   **Figure 4- Summary of elements found by sample**

434   **Figure 5- GeO2 nano-crystals found in sample A after evaporation**

435   **Figure 6- COD results by sample before and after ultra-filtration and coagulation/flocculation**

436   **Figure 7- Titration curve for sample F**

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