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ABSTRACT

One factor influencing the efficiency of KDP frequency conversion arrays on the Nova laser system at LLNL has been environmental degradation, or "fogging", of the crystal surfaces. Decreases in array transmission by as much as 20% have been attributed to crystal fogging. The surfaces of the 27-cm square Nova array crystals are prepared by a wet diamond-turning process. The rate of surface fogging has been associated with several parameters of the diamond turning and subsequent cleaning processes. High humidity during diamond turning, storage, and use on the laser tends to accelerate the fogging. We suspect that some of the additives present in the diamond turning oil increase the fogging rate and have found a machining oil which minimizes this surface degradation. Efficient removal of the machining oils from the crystal surface also minimizes the fogging problem. Care must be taken to use cleaning solvents which do not cause additional surface degradation. The fogging rate is sensitive to the crystallographic orientation of the material as well as to surface roughness related to the diamond turning process. Accelerated fogging at diamond turning artifacts may increase crystal surface roughness causing increased beam modulation and scattering losses.

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1. INTRODUCTION

On the Nova laser system at LLNL frequency conversion of the laser beam wavelength from 1.05 μm to 0.35 μm is obtained by transmission of the beam through a pair of potassium dihydrogen phosphate (KDP) non-linear crystals. The surfaces of the crystals are prepared by wet-diamond turning and are then coated with a with a sol-gel SiO_2 AR coating prior to installation. One factor influencing the efficiency of this conversion is the environmental degradation, or "fogging", of the crystal surfaces. Figure 1 shows an example of the scatter produced by a fogged KDP crystal surface. Decreases in array transmission of as much as 20% have been attributed to crystal fogging. Figure 2 shows the degradation of 0.35 μm light transmission over time for crystal arrays on six of the ten Nova beamlines. The time averaged rate of degradation ranged from 0.18 to 0.38%/month with an average of 0.28%/month.

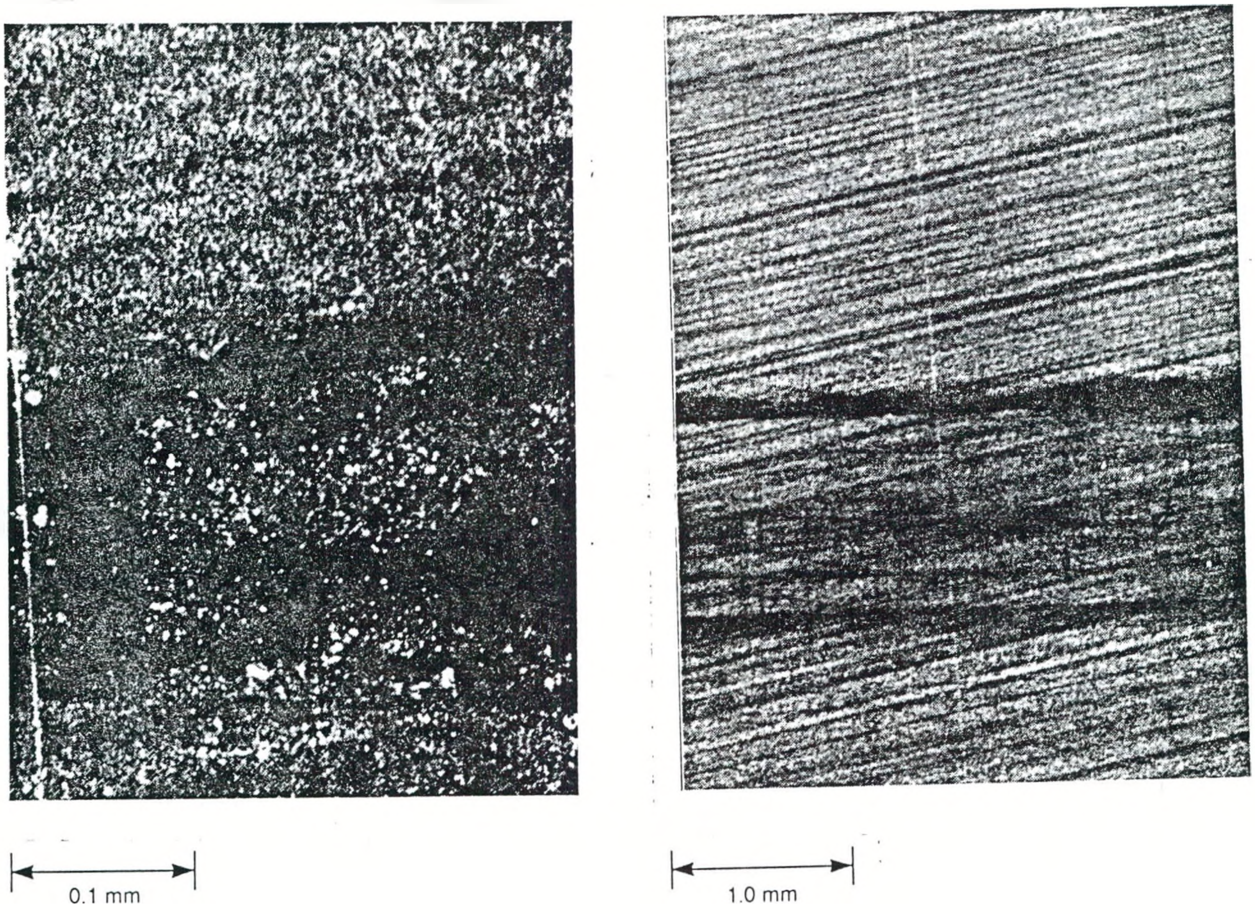


Fig. 1. Optical micrographs, at two magnifications, of the "fogging" induced scattering on the surface of a KDP crystal removed from the Nova laser system. Note how the fogging makes the diamond turning tool tracks visible.

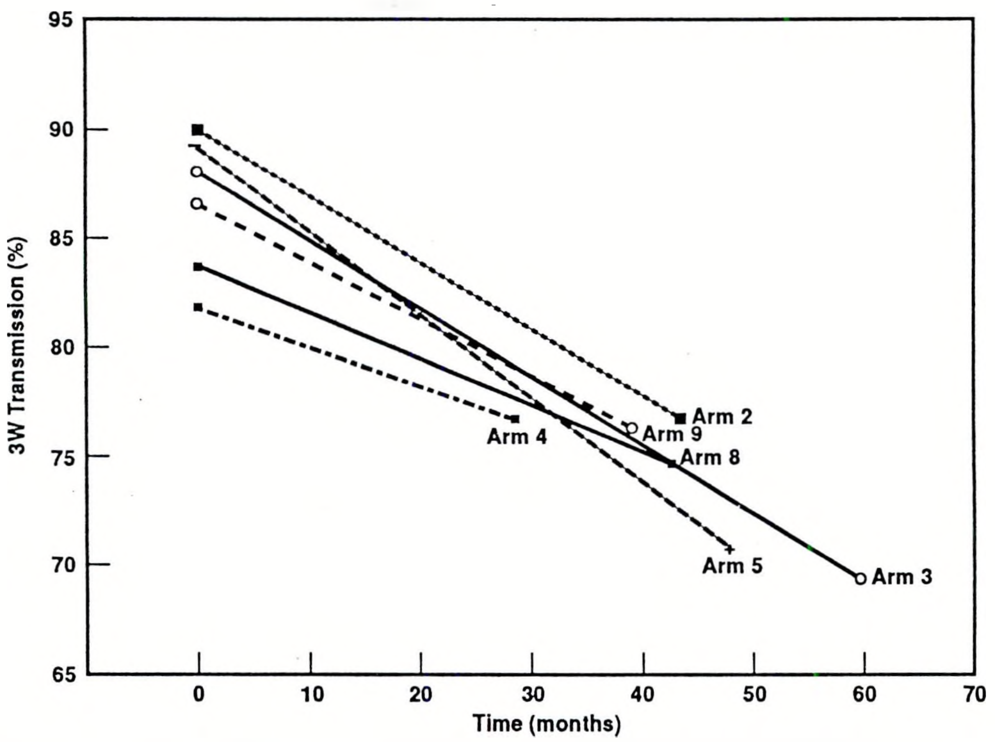
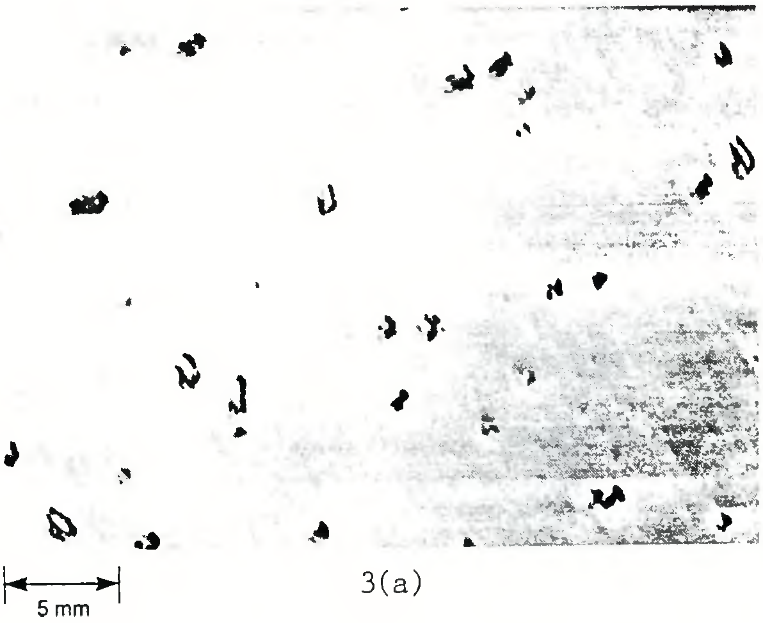


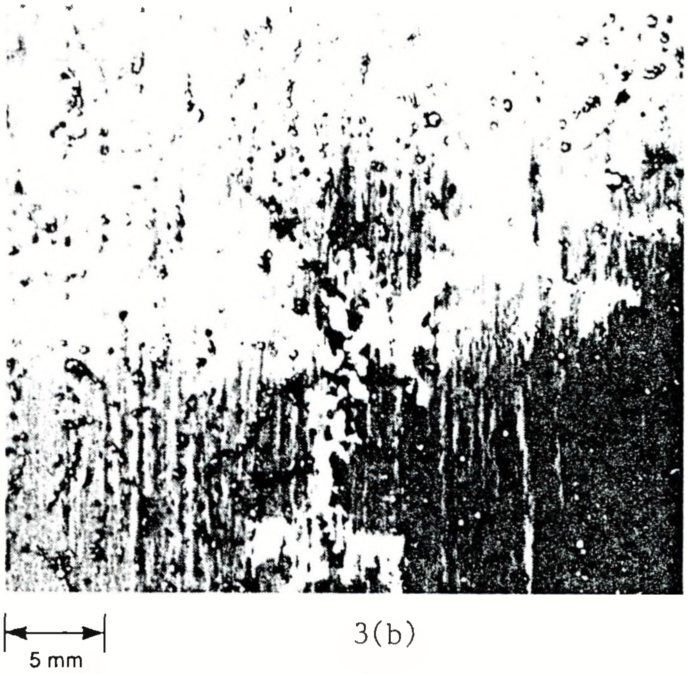
Fig. 2. Plot of 0.35 μm transmission degradation through the frequency conversion arrays on six of the Nova laser beamlines.

Observations accumulated over the years have suggested that the fogging phenomenon is related to the machining oils to which the crystals were exposed during diamond turning or to environmental effects (humidity, air flow) during storage and use. During diamond turning the crystals are cooled and the machine is lubricated using a low molecular weight shower oil. The X-Y stage slides are lubricated using a high molecular weight way oil. During machining the heavy oil splashes into the light oil resulting in an approximately 2:1 mix of light:heavy oil ('mixed oil'). After diamond turning the crystals are cleaned at the manufacturer by a toluene dip and soak process. The crystals are again cleaned prior to sol-gel coating at LLNL using a toluene soak, dip, and 80 psi spray process. While on the beamline the crystals are exposed to ambient temperatures and relative humidities of < 50%.

The fogging of the crystals is very sensitive to the environment. Some crystals have been kept on desks for years without fogging while others have fogged overnight when stored in a fume hood. Condensation of water vapor onto the crystals will surely cause some surface degradation. Fogging degradation generally appears as a haze on the surface. Under light microscopy the fog often appears to consist of micron scale scatter points. Under the higher magnifications of electron microscopy the fogging takes many forms. In most cases the fogging features appear as rough cylindrical particles of ~ 3 μm in length as shown in Fig. 3a. Other structures observed include what appears to be a dendritic growth (Fig. 3b). The range of structures associated with KDP crystal fogging indicates that several mechanisms are responsible for this degradation process.



3(a)



3(b)

Fig. 3. SEM micrographs of two types of fogging structures observed on KDP crystals: (a) cylindrical particles, and (b) dendritic growth.

Potassium dihydrogen phosphate, KH_2PO_4, is an acid salt of phosphoric acid, H_3PO_4. The crystal consists of a 3D array of $PO_2(OH)_2^-$ ions connected by hydrogen bonds. The diprotic ion can either gain or loose a H^+ ion and can therefore act as either a base or an acid, respectively. Such dual reactivity crystals are described as amphiprotic. The crystal has a pH of 4.4-4.7.[1] Chemical handbooks appear to be split as to whether KDP is hygroscopic, but it does have a high solubility in water. The confusion over its hydrophilic properties is probably related to a strong dependence of surface reactivity on surface contamination and structure.

The reactivity of KDP to atmospheric water has been demonstrated by Hirsch and Adams.[2] They showed that when a KDP surface was damaged by ion bombardment in vacuum the surface was made reactive. Upon bringing the crystal to ambient conditions the surface would react with water vapor producing a "corrosion" reaction. Their description of "rod like" corrosion products with micron scale lengths agrees with our observations on diamond turned crystals. Hirsch's work suggests that a perfect KDP surface is not reactive to atmospheric water but that the surface can be activated by structural damage.

Results presented in this paper show that the fogging phenomenon is associated with several parameters of the diamond turning and subsequent cleaning processes. The study included chemical analysis of the machining oils, surface analysis of the KDP crystals, and controlled fogging experiments under various conditions. As a result of this work several changes have been made in KDP machining and handling procedures.

2. PRELIMINARY CONTROLLED FOGGING TESTS

Initial experiments were designed to determine if humidity and machining oils did in fact influence crystal fogging rates. The first set of experiments tested six 1-in. square crystals that were diamond turned at LLNL using either the shower, way, or mixed oil (2 crystals each). After diamond turning the samples were dip cleaned in toluene and stored in a clean room under high air flow. The cleaning method was a scaled-down version of that used in the manufacturing process. Prior to storage the crystals were examined visually using bright-light illumination and using 50X and 107X Nomarski microscopy. Polaroid photography was used to document the state of the crystal surface during the tests. No sign of fogging was present on the crystals initially. The crystals were then reexamined using Nomarski microscopy after periods of one week. The observations made over a periods of 6 weeks are shown in Fig. 4. The relative degrees of fogging reported are based on the apparent density of artifacts on the crystal surface. The fogging rates are too slow to produce measurable changes in transmission during the test period. No fogging was observed on any of the crystals after 1 week. After 3 weeks samples machined in shower oil were fogged. Also, one mixed oil sample showed some fogging. After 5 weeks the two way oil samples showed some minor fogging. shower oil samples showed the heaviest fogging during all stages of the test. Fogged crystal surfaces from these tests consisted of 3-6 μm size structures. The density of these features was about 1000/cm^2. These tests indicated that the shower oil produced the highest rate of KDP surface fogging.

Another set of crystals was prepared in order to determine the influence of humidity on the fogging rate. Four 1-in square samples were diamond turned in the mixed oil and one sample was turned in the shower oil. The samples were dip cleaned in toluene and then examined as in the oil comparison tests above. The crystals were than stored in chambers with humidity levels of 80%, 44%, and 0% RH. These chambers were glass desicators containing saturated solutions with the appropriate vapor pressures.[3] Two mixed oil samples stored at 80% RH were fogged after 3 days. Fogging did not get much worse after an additional two weeks. Mixed oil samples stored at 44% and 0% RH had not fogged after two weeks. The sample diamond turned in shower oil and then exposed to 80% humidity showed the highest degree of fogging after only one week. At magnifications of 100X the fogging had an 'orange peel' morphology. At 440X the fogging appeared to be many small 'bumps' about 5-10 μm in diameter.

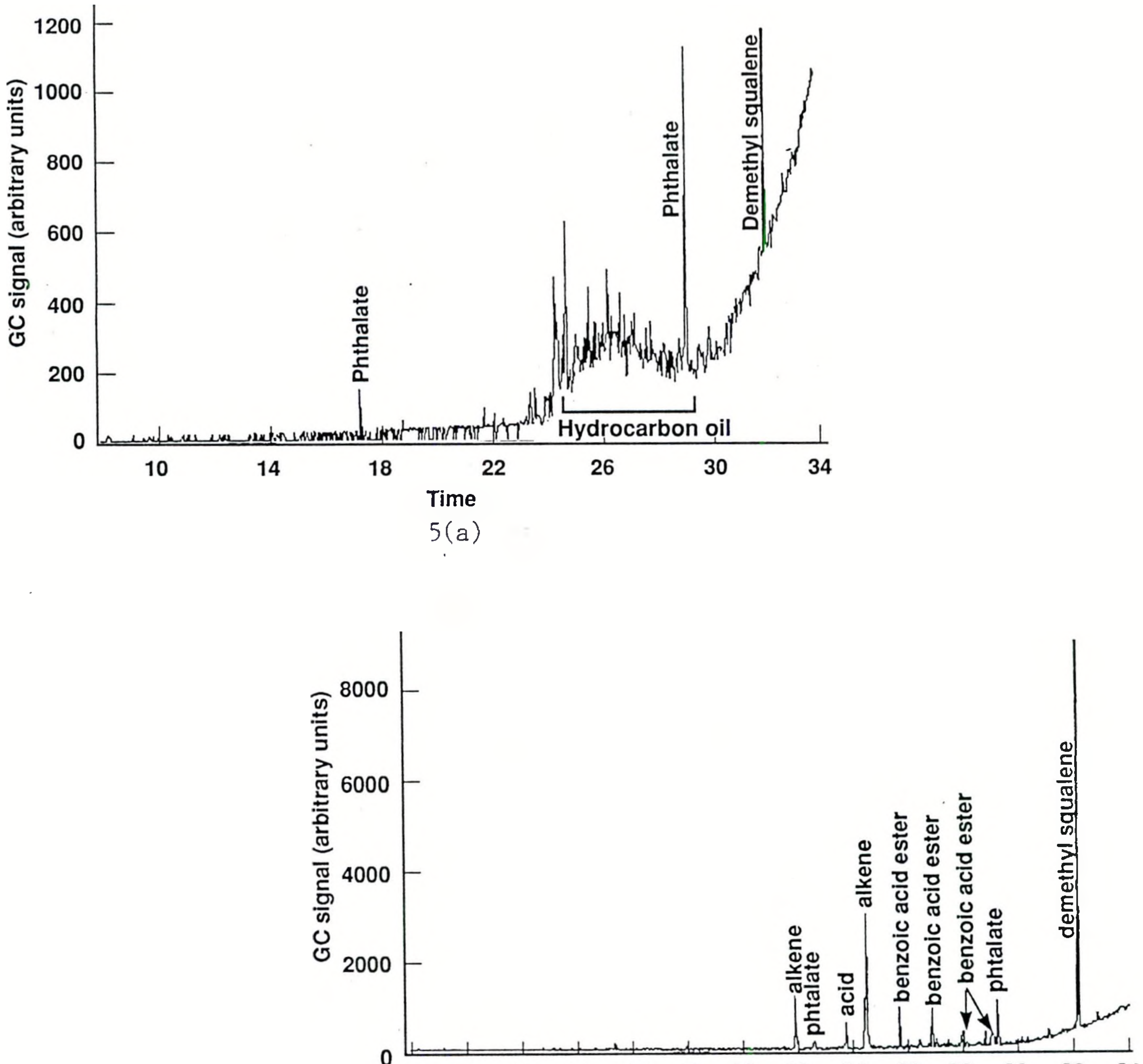
Oil Test:		**1 week**	**3 weeks**	**5 weeks**
	shower	—	⬤	◉
	way	—	—	●
	mixed	—	•	●
Humidity Test:				
mixed	**80%**	⬤	⬤	⬤
	80%	⬤	⬤	⬤
	44%	—	—	—
	0%	—	—	—
shower	**80%**	⬤	⬤	◉

No fogging — • ● ⬤ ◉ **Heavy fogging**

Fig. 4. Table showing the relative amounts of fogging observed during controlled fogging tests on freshly diamond turned KDP crystals.

One additional sample was diamond turned in the mixed oil and then left immersed to oil for over 20 hours. This sample was then dip cleaned in toluene. The side of the crystal not facing the chuck was heavily fogged. One edge of the crystal showed extra heavy fogging. The latter observation may be due to a large bead of oil formed at the bottom edge of the crystal as the oil drains. The side facing the chuck showed little or no fogging. The fogging morphology was similar to that observed in the oil/humidity tests.

The tests described above indicate that the fogging rate is influenced by the diamond turning oils with the highest fogging rate being observed for the shower oil. Fogging at high humidity levels shows that the water is a key component of the fogging reaction.



5(a)

5(b)

Fig. 5. GCMS spectra of a solution obtained by rinsing a KDP crystal with methylene chloride. (a) as-received, (b) after cleaning with toluene.

3. CHEMICAL ANALYSIS OF CRYSTAL SURFACES

In order to determine if residual oil was present on the crystals after cleaning a crystal surface was analyzed as-received from the manufacturer. The surface was rinsed with methylene chloride and the rinse solution was analyzed by gas chromatography mass spectroscopy (GCMS). The resulting spectra shown in Fig. 5a showed that residual oil was in fact present. With further toluene cleaning (see section 5.) this oil could be removed from the crystal surface (Fig. 5b). Other organic contaminants present were plasticizer compounds such as phthalate and benzoic acid ester. Analysis of fogged crystal surfaces using EDS and electron microprobe analysis showed no clear difference, in composition or stoichiometry, between fogged and not fogged crystals or between the fogging particles and the background material on the fogged crystals. Sporadic contamination by Al, Ca, Cl, Na, Si, and Zn was observed, but these contaminants could not consistently be correlated to the surface fogging. These results agree with earlier studies of as-received KDP crystals by x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) which showed that the major contaminant on the KDP crystal surface was hydrocarbons but that trace Na and Zn could also be found.[4]

4. CHEMICAL ANALYSIS OF DIAMOND TURNING OILS

GC analysis of the oils showed that the shower oil and the way oil both contained a wide molecular weight band of hydrocarbons and that the band for the way oil was ~ 35% heavier than was the shower oil. These pure hydrocarbons should not react with the KDP crystals. The oils did, however, contain a number of additives. The shower oil contained an oxidation inhibitor (metal salts), a pour-point depressant (polybutene), and an anti-wear agent (nitrogen based), while the way oil contained an antiwear agent (silicone based) and a tackiness agent (rubber). Inorganic analysis of the oils showed that the major components of the oxidation inhibitor were organic salts of Zn, Ca, and P.

The surface of KDP consists essentially of -P-O-H groups and should behave chemically similarly to phosphoric acid, H_3PO_4. We therefore qualitatively tested the reactivity of the oils to phosphoric acid. 20 ml of the way and shower oils were added to separate vials containing 20 ml of H_3PO_4. As the oil and acid are immiscible, the mixture was stirred for two days and than separated using a centrifuge. The separated acid showed an obvious change in color for both oils. For the way oil the acid was light yellow while for the shower oil the acid was dark brown. A pure mineral oil was also mixed with the acid. The pure oil showed little or no reaction with the acid. This test therefore suggested that it was the additives in the oil that were reactive to the KDP surface.

We also carried out a test in which the shower oil was stirred with powdered KDP for 24 hours. Quantitative analysis of the oil before and after treatment indicated that the calcium content had been reduced from 109 ppm to 81 ppm and zinc from 560 ppm to 368 ppm. These results show that Zn and Ca are leached from the oil by KDP and it is likely that they form phosphates on the surface by reaction with the free acid groups. Both calcium and zinc phosphates are known to form hydrates which could contribute to the fogging problem.

As a result of these tests a pure mineral oil is now used to diamond turn KDP crystals for the Nova laser system. The change of oils has noticeably reduced the occurrence of fogging on freshly turned crystals.

4. INFLUENCE OF SURFACE STRUCTURE

Part of the irreproducibility of fogging experiments is likely related to a dependence on surface properties. Fogging rates for controlled tests were greatest when freshly turned surfaces were exposed to humid environments. The fogging rate was much slower for crystals that were exposed to ambient conditions for several days prior to exposure to humidity. We propose that the absorption of contaminants at reactive sites may slow the fogging reaction.

The fogging rate is also dependent on surface roughness. Fogging was often must significant along diamond turning lines or scratches. The fogging made these features much more visible (see for example Fig. 1) and may therefore contribute to degradations in beam uniformity caused by diamond turning artifacts. In some cases beam modulations from the crystal surface have been so significant on the Nova system that optics downstream from the crystal have shown laser damage patterns that match the KDP diamond turning patterns. Hirsch and Adams[2] also reported increased corrosion at scratches and attributed this to high concentrations of catalytically active sites at surface irregularities.

Fogging rate was also dependent on the direction of diamond turning tool movement relative to crystallographic orientation. Two KD*P (KD_2PO_4) crystals were cut with surface planes parallel to the crystal z-axis. For one crystal the surface was diamond turned with the tool motion perpendicular to the z-axis, while for the other crystal the tool moved parallel to the z-axis. For two pairs of crystals the sample turned parallel to the z-axis showed a higher rate of fogging.

5. CLEANING OF DIAMOND TURNED KDP CRYSTAL

KDP crystal cleaning procedures have been developed in order to maximize the removal of diamond turning oils which influence fogging and also to remove contaminants which affect AR coating quality. The cleaning procedures consist of several stages of dipping, drag wiping, and spraying with toluene as listed below:

Cleaning process immediately following diamond turning:

1. Blot oil off surface with lens tissue.
2. Dip crystal into three successive toluene tanks.
3. Place plastic film wrap on crystal, smooth wrinkles, and than remove.

Repeat on other side of crystal. This process removes KDP dust and aluminum chuck residues.

4. Blow crystal dry off N_2 treated with an anti-static gun. The anti static-gun reduces static charge on the crystal surface.
5. Drag wipe with toluene.
6. Remove remaining residues with cotton swabs.
7. Toluene dip soak crystal for 10 minutes.

After drying, the crystals are vacuum bagged for shipment. The vacuum bagging reduces the influence of humidity on the crystals during shipment and storage.

Cleaning process upon receipt of crystals at LLNL:

1. Toluene soak for 16 hours. Check for sheeting on surface during removal. Solution sheeting is required for good coating adhesion.
2. 80psi spray with toluene.
3. Drag wipe with toluene soaked lens tissue.
4. Soak for two hours in toluene. Check for sheeting during removal.
5. Repeat steps 2 and 3.

We attempted to substitute tetrachloroethylene for toluene in the cleaning process at LLNL. This change in solvent resulted in accelerated hazing of the crystals. It was determined that the tetrachloroethylene decomposes during storage to form trace amounts of HCl. The acid reacts with the amphiprotic KDP resulting in a type of fogging. In contrast to the other types of fogging discussed above, the tetrachloroethylene fogging could be removed by recleaning the surface with toluene. The fogging particles in this case were likely KCl crystals.

6. INFLUENCE OF COATINGS ON THE FOGGING RATE

KDP crystals used in the Nova frequency conversion arrays are commonly coated with a sol-gel SiO_2 single layer anti-reflection coating. This coating does not appear to significantly influence the fogging rate. The sol-gel coating is not expected to provide an effective barrier to moisture because of its porous nature. It should be noted however that the sol-gel suspension is prepared using an ammonia catalyst. If the ammonia is not removed from solution prior to coating surface fogging occurs. The fogging is probably the result of ammonia phosphate formation. Before coating the crystals we therefore remove the ammonia from solution using a 24 hour reflux process.

In 1984 a KDP crystal on Nova was coated with a silicone film in an effort to reduce small angle scatter. This silicone coating has proven over the last five years to protect the KDP surface from fogging. The measured rate of an uncoated crystal is 7.3% over a 36 month period (i.e. 0.2%/month) vs. 2.1% for the silicone coated crystal (0.06%/month). Also, much of the loss on the silicone coated crystal was regained by spray cleaning with toluene. Details of the silicone coating properties and procedures are given in another paper in this session.[5] The silicone coating is now used on all new or reworked crystals put into the Nova laser system.

6. CONCLUSIONS

Degradation of KDP crystal surfaces after diamond turning has been associated with metal-based additives in the diamond turning oils and to contact with humid environments. A pure mineral oil is now used in the KDP diamond turning process. The use of the new oil has noticeably reduced the occurrence of fogging on freshly turned crystals. Crystal cleaning procedures have also been improved to minimize oil contamination on the crystal surfaces. The influence of humidity on the crystals is minimized in the laser system by the application of a protective silicone coating.

7. REFERENCES

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