AO 1400 Antioxidant and Hot Melt Adhesive Performance Review

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Abstract

The new antioxidant AO 1400 is compared with the AO 1010 powder and AO 1010 free flow (FF) forms. Due to its unique physical form, AO 1400 exhibits better flowability and can eliminate bridging problems during feeding. It also generates less dust during feeding and handling to help provide better workplace hygiene as compared to the AO 1010 powder and FF forms.

This study compared the antioxidant chemical and physical properties, and includes videos illustrating their feeding characteristics. Particle size distribution and dust explosion test results were also compared. The three antioxidants were then tested in hot melt adhesive formulations with mixing and coating to produce adhesive laminates, and adhesive performance was tested before and after aging. All three AO's were found to provide comparable stabilization performance.

Introduction

Both synthetic and natural polymers can undergo oxidation reactions when exposed to air. Polymers are subject to oxidation during their entire life cycle: manufacturing, processing, storage, and end use. Elevated temperatures, irradiation, and catalysts like metal ions increase oxidation rates. Very low levels of oxidation can have a great impact on material properties. The effects of oxidation on a polymer's chemical structure are collectively termed as "degradation". Most polymers contain structural elements prone to oxidative degradation reactions. For adhesive materials, degradation can change viscosity, color and other physical properties, and thus adhesive performance as measured by tack, adhesion and cohesive strength are changed, especially after aging.

The reaction of organic compounds with molecular oxygen is called autooxidation, which proceeds by a series of free-radical initiated chain reactions. Antioxidants are used to trap these radicals and other intermediates (such as hydroperoxides), thereby protecting materials from oxidation and the resulting loss of physical, mechanical or optical properties.

Primary antioxidants are hydrogen donors which function by converting peroxyl radicals to more stable hydroperoxides. Commonly used primary antioxidants include the sterically hindered phenols, for example AO 1010, the chemical structure of which is shown in Figure 1.

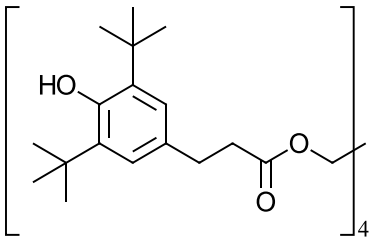

Figure 1: AO 1010 chemical structure

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AO 1010 is widely used in the stabilization of adhesives and polymers. Previously, AO 1010 was available in two different physical forms: A powder form (AO 1010) and a free-flowing, granular form (AO 1010 FF). The powder form disperses easily during adhesive formulation but tends to have poor flowability characteristics, leading to problems like bridging in feeders. To enhance the flowability and reduce bridging, the free-flowing, granular FF form was developed. Recently a micro-beads form of the product, AO 1400, was developed with the goal of reducing dust generation during feeding and handling to enhance workplace hygiene. This paper documents the findings when these three different physical forms were compared.

Chemical identification

Figure 2 compares the FT-IR spectra of AO 1010 powder and AO 1400. Clear differences between the two products were observed. While the root cause of the difference was not investigated in this study, it is considered that crystallinity variation between the products contributed to the differences.

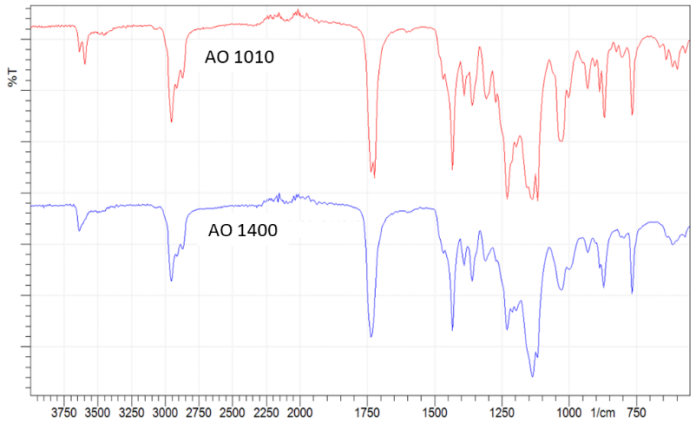


Figure 2: FT IR spectra comparison of AO 1010 and AO 1400

HPLC testing confirmed AO 1010 and AO 1400 to be chemically identical, as shown in Figure 3.

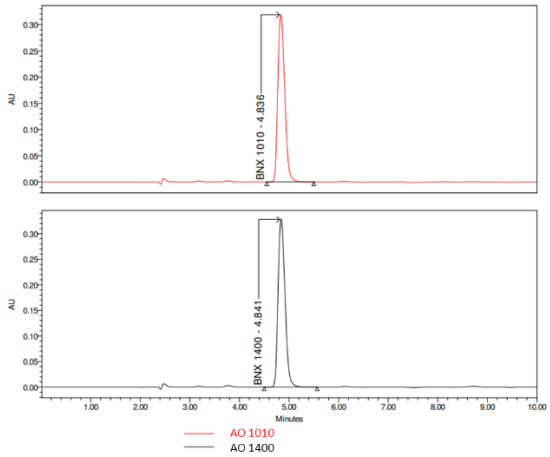


Figure 3: HPLC test comparison of AO 1010 and AO 1400

Differential Scanning Calorimetry study

Figure 4 presents an overlay of five DSC scans including AO 1010, AO 1010 FF and AO 1400. While AO 1010 and AO 1010 FF show similar single melting endotherms, AO 1400 shows two distinct endotherms. It was also noted that the heat of fusion (ΔH_f) associated with melting in AO 1400 was significantly lower as compared to AO 1010 or AO 1010 FF. It was originally considered that the powder product form should have fast dispersion during processing due to its fine particle size, but the broader melting range and lower heat of fusion of AO 1400 are conducive to fast dispersion as well.

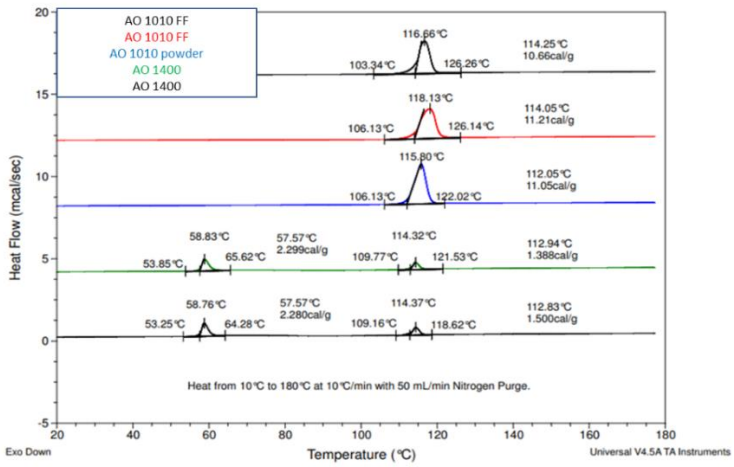


Figure 4: DSC studies of AO 1010, AO 1010 FF and AO 1400

Flow testing

These three products were compared in a flow/feeding test shown in Figure 5. Under the same test condition AO 1010 and AO 1010 FF generated visibly more dust at feeding than AO 1400. Also bridging in the funnel was observed during feeding of AO 1010 in powder form.

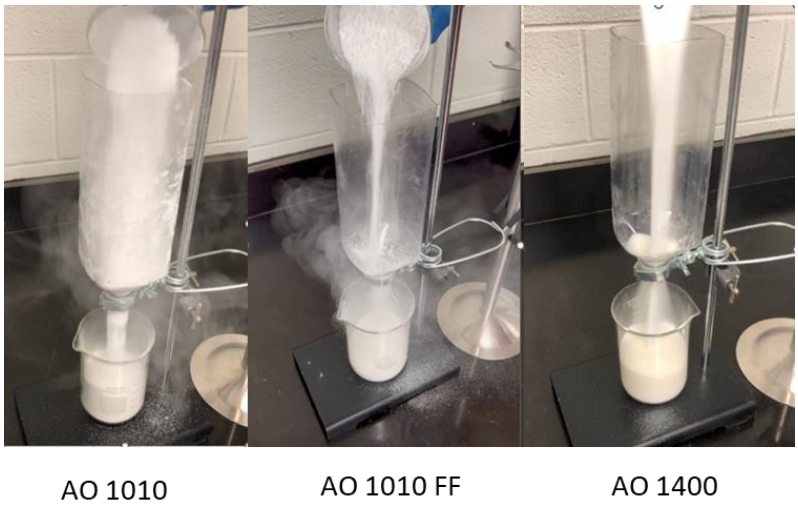


Figure 5: Antioxidant feeding tests.

Particle size distribution

Particle size distribution is an important characteristic of solid chemicals, as it influences material flow and conveying behavior, and affects reactivity, production hygiene and safety, etc. Particles that are smaller than approximately 100 μm in diameter can be released into the air during handling and feeding operations. Conveying and handling can also induce attrition and abrasion by which smaller particles are produced, thereby increasing the potential for dust generation. The material size, shape, process type, handling speed, and material properties impact dust characteristics and dust generation.

Respirable and inhalable dust particles affect the body in different ways, posing a unique set of risks depending on particle size. Being able to accurately measure these different sizes goes a long way toward maintaining a healthy working environment.

Inhalable dust refers to particles as large as 100 μm in diameter, that can be inhaled into the nose or mouth. Respirable dust refers to particles measuring 10 μm or less in size. These particles are much finer, almost invisible to the naked eye. They stay airborne longer and can penetrate deep into the bronchioles of the lungs.

Combustible particulate solids with a minimum dimension greater than 500 μm generally have a surface-to-volume ratio that is too small to pose a deflagration hazard. 500 μm is now considered an appropriate size threshold for combustible dusts, and spherical particles greater than 500 μm in diameter are generally not considered deflagratory.

Particle size distribution of a combustible particulate solid is an important parameter in accessing an explosion hazard, Particle size implies a specific surface area and affects the numerical measure of dust explosion parameters, which are covered in more detail in the next section.

In the current study, particle size distribution was measured and compared as shown in Figure 6. It can be seen that significantly higher levels of respirable particles up to 10 μm in diameter are present in AO 1010 and AO 1010 FF as compared to AO 1400. These two products also contain significantly higher amounts of inhalable dust up to 100 μm. AO 1400 has a tighter particle size distribution, which might contribute to dispersion and process optimization.

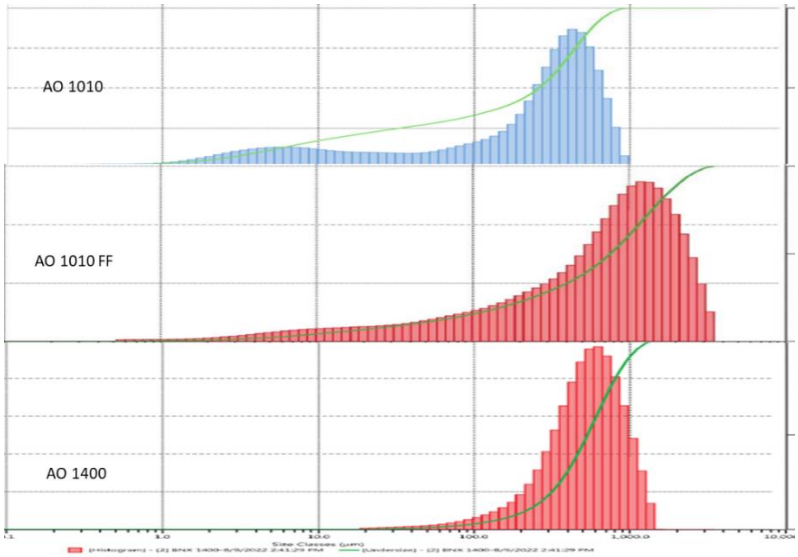


Figure 6: Particle size distribution analysis of AO 1010, AO 1010 FF and AO 1400

Dust explosion test data

Table 1 presents test data on Minimum Ignition Energy (MIE), Minimum Explosible Concentration (MEC), and Explosion Severity. Please note that the values obtained are specific to the sample tested as well as the exact method and equipment used. The values are not to be considered intrinsic material constants. Any change in particle size, shape, volatility or moisture content may change the results.
The Minimum Explosible Concentration is the minimum concentration of a combustible dust that is capable of propagating a deflagration through a uniform mixture of the dust in air, under the specified conditions of the test. The MEC data can provide a relative measure of the concentration of a dust in the form of a uniform cloud necessary for an explosion. In general, higher MEC values indicate a reduced risk of fugitive dust explosions and explosions in dilute phase pneumatic transport. Lower MEC materials are more hazardous in that low concentrations of dust dispersed in air present are explosible with an ignition source present. Higher fugitive dust explosions may also pose a risk once an initial explosion occurs with the presence of a combustible dust or powder in the area. It is recommended that concentrations be kept at a minimum (i.e., by routine housekeeping to remove fugitive dust), otherwise explosion venting and inerting or nitrogen suppression may be needed.

The MEC value for AO 1400 was determined to be between 30 g/m³ and 40 g/m³ with an interpolated value of 34 g/m³. It is important to keep dust concentrations below the MEC in order to minimize the risk of a dust explosion.

The Minimum Ignition Energy (MIE) test determines the minimum ignition energy of a dust cloud in air by a high voltage spark. Results for AO 1400 indicate that the sample tested has an MIE value that is greater than 1000 mJ. Most electrostatic ignition sources have energies less than 1000 mJ. Common electrostatic ignition sources are typically less than 30 mJ (people, small, isolated components, etc.). Grounding and bonding of process equipment is still recommended. NFPA 654, 652, 77, 68, and 69 can provide proper guidance and instructions.

The Deflagration Index, K_{St} is the average maximum pressure rise (dP/dt) normalized to a 1.0-m³ volume. It is measured at the optimum dust concentration. The (dP/dt)max is the average maximum value for the rate of pressure increase per unit time reached during the course of a deflagration for the optimum concentration of dust tested.

In conclusion, while AO 1400 generates less dust during handling and feeding than the other forms, the explosion test data indicate that sufficient volumes of small particles dispersed in air are still explosible. Therefore, as with the powder and FF forms, precautions must be taken during use to mitigate the explosion hazard, including but not limited to routine housekeeping to control dust generation and accumulation, bonding and grounding of containers and equipment, and eliminating potential sources of ignition. As the hazards present in each workplace are unique, assessment of the dust explosion hazards by a qualified professional is recommended.

Table 1: Explosion test data

Test items	AO 1010 powder	AO 1400
MIE, mJ, Minimum Ignition Energy with inductance ASTM E2019	1<MIE<4 Es=1.4	MIE>1000** Es not determined
MEC g/m3, Minimum Explosible Concentration ASTM E1515	Expecting	30<MEC<40 MEC est = 34
Kst bar-m/sec, Deflagration Index, ASTM E1226	211±10%	187±12%
St Class	St 2 class	St 1 class
**1000 mJ is the maximum energy the MIKE3 is capable of discharging		

Hot melt adhesive stabilization testing

The three antioxidants were tested in a typical hot melt adhesive formulation.

Experimental

Raw materials

- Mineral oil
- C5 hydrocarbon resin
- SIS Rubber
- Antioxidants: AO 1010, AO 1010 FF, AO 1400

SIS rubber PSA formulations:

Table 2 lists the four hot melt adhesive formulations being mixed, cast, and tested in this study.

Table 2: Hot melt adhesive formulations.

Hotmelt Adhesive Formulation	Control	AO 1010	AO 1010 FF	AO 1400
SIS rubber	37	37	37	37
C5 resin	49.5	49.5	49.5	49.5
Mineral oil	13	13	13	13
AO 1010, 1010FF and 1400	0	0.5	0.5	0.5

Typical adhesive mixing process:

1. SIS rubber was weighed out into a 1 gallon can with the antioxidant. The can was rolled for 2 hours at 6 rpm to achieve uniform mixing.
2. A small Paul O. Abbe sigma blade mixer with hot oil heating jacket was used for mixing and preheated using a hot-oil setpoint temperature of 380°F.
3. The rubber mixture with AO was added to the mixer and blended for 20 minutes.

4. C5 resin was added to the mixer and blended for 20 minutes. The hot oil set-point temperature was lowered to 240°F and the sides and lid of the mixer were scraped before re-starting the mixer for 5 more minutes.
5. The Mineral oil was then added to the mixer and blended for 15 minutes.
6. The finished adhesive was poured from the mixing bowl into a Pyrex glass dish.

Four batches of hot melt adhesive were prepared in this manner: three with additional antioxidants and the antioxidant-free control formulation.

Adhesive coating process:

A ChemInstruments HLCL-1000 hot melt adhesive coater was used to apply hot melt adhesive to the silicone release side of the polyester sheet. The coating conditions were as follows:

- Coat on silicone side of 2 mil PET film
- Cover adhesive with 4.5 mil L-3 easy release liner
- 375°F Adhesive melting oven temperature

A 15-to-20-foot length of adhesive, approximately 1.3 mils thick (32 g/m^2) was produced from each of the four adhesive formulas.

Adhesive lamination:

For peel adhesion, static shear and loop tack testing, sheets were laminated to 2 mil polyester (PET) films using a bench top laboratory laminator. The adhesive was laminated to an untreated 2 mil PET using ~20 psi lamination pressure.

Adhesive testing:

Peel Adhesion
Peel adhesion was determined according to the ASTM D3330 Method A using a ChemInstruments AR-1000 Adhesion Release Tester with the EZ Lab software program. One inch (1.0”) wide samples were applied to a standard stainless-steel substrate at a rate of 24 in/min with a 4½ pound rubber covered roller according to the method. The tape was then peeled from the substrate at a 180° angle at 12 in/min after a dwell time of one minute. The force required for removal was measured, averaged, and the mode of failure noted. Five replicates of each sample were tested before and after aging.

Static shear
Static shear was determined according to the ASTM O3654A test method using a ChemInstruments RT-30 Shear Tester. A 1.0” x 1.0” sample was applied at room temperature to a 2" x 3" panel with a 4½ pound rubber covered roller at a rate of 24 in/min according to the test method. An aluminum clip to evenly distribute the applied load was attached to the free end of the sample. The panel with the sample was placed in the shear test stand. After a dwell time of one minute, a 1.0 kg mass was hung from the clip. Timing began when the weight was positioned on the sample, and automatically stopped when the sample slipped from the panel. The time and the mode of failure were recorded. Five replicates of each sample were tested before and after aging.

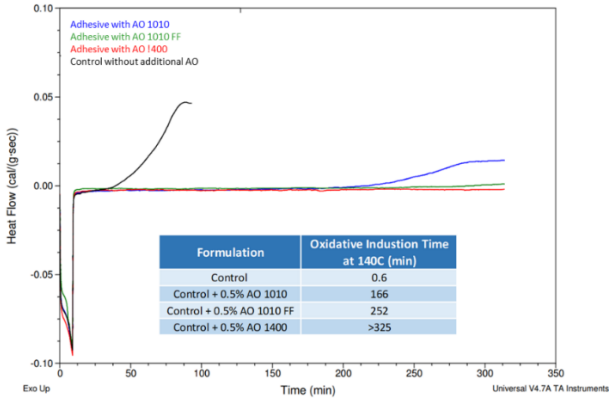
Loop tack
Loop tack was tested according to the ASTM D6195 test method using a ChemInstruments LT-1000 Loop Tack Tester. A 1" x 5" sample was prepared, then formed into a loop with the adhesive exposed on the outside. Masking tape was used to hold the loop together at the top. The loop was placed in the tester and lowered at a rate of 12 in/min toward the substrate below. The adhesive made a 1 square inch contact area with the substrate. When the travel of the jaw bottomed, the direction was automatically reversed. As the adhesive was pulled from the substrate, the maximum force observed during its removal was recorded. Five replicates of each sample were tested before and after aging.

Aging and Test Conditions
The adhesive samples were placed in 60ºC oven for 4 weeks to simulate aging under ambient conditions for 1 year. All testing was performed at standard conditions, 73±3°F and 50±% RH.

Results and discussions

Compared to many rubber PSA formulations, the current formulation is expected to be inherently robust with respect to heat aging. The mineral oil used in formulation is a white mineral oil that is a mixture of linear, branched or cyclic alkanes which are only weakly reactive and possess good oxidation resistance. SIS rubber is supplied with primary and secondary antioxidant package up to 0.2% (w) each. When heat aged, its polyisoprene chains undergo chain scission, leading to loss of tensile strength and elongation. The aliphatic C5 hydrocarbon resin is stabilized by addition of 0.1% (w) antioxidant. In general, aliphatic C5 resins have better aging resistance than other tackifying resins such as rosin esters, tall oil, or terpenes.

Oxidative Induction Time
Oxidative Induction Time (OIT) can provide a quick indication of antioxidant power left in an adhesive after processing. OIT results were determined at 140ºC and are summarized in Figure 7. The control adhesive formulation without additional antioxidant started to oxidize after only 0.6 minute, indicating that the antioxidants inherited from the SIS rubber and tackifer were nearly consumed during the mixing process. When additional antioxidant was added to the adhesive, all three formulations showed much longer times before oxidative breakdown was initiated. The higher OIT result for the formulation containing AO 1400 was unexpected.



Formulation	Oxidative Industion Time at 140C (min)
Control	0.6
Control + 0.5% AO 1010	166
Control + 0.5% AO 1010 FF	252
Control + 0.5% AO 1400	>325

Figure 7: OIT test results comparison of mixed hot melt adhesive

Peel, loop tack and shear test

The test results for 180º peel, loop tack and static shear test results are summarized in Table 3.

Table 3: Hot melt adhesive test data.

Sample	Control formulation		AO 1010		AO 1010 FF		AO 1400	
Coat weight (mil)	1.3		1.3		1.3		1.3	
Facestock	2 mil PET		2 mil PET		2 mil PET		2 mil PET	
180 Peel 1min Dwell	**lb/in**	**FM**	**lb/in**	**FM**	**lb/in**	**FM**	**lb/in**	**FM**
ASTM D3330 A, SS	6.1±1.0	C4A6	5.7±1.0	C1A9	4.0±0.4	A	3.8±0.2	A
After 1 year aging	6.0±0.8	C2A8	5.0±1.2	A	5.6±2.0	C4A6	4.5±0.6	A
Loop Tack	**lb/in**	**FM**	**lb/in**	**FM**	**lb/in**	**FM**	**lb/in**	**FM**
ASTM D6195, SS	6.4±0.8	A	6.4±0.6	A	6.3±0.9	A	5.3±0.3	A
After 1 year aging	7.2±0.6	A	5.9±1.1	A	5.6±0.7	A	5.4±0.5	A
Static shear	**Mins**	**FM**	**Mins**	**FM**	**Mins**	**FM**	**Mins**	**FM**
ASTM D3654A, 1" x 1" x 1kg, SS	6085±1008	A	4195±855	A8T2	7637±3249	A9T1	4275±1700	A9T1
After 1 year aging	2953±1211	C	6937±1745	C	10081±3395	C	7341±2976	C
Table keys:								
FM: Failure Mode			A9T1: 90% adhesive failure, 10% transfer					
C4A6: 40% cohesive failure, 60% adhesive failure			SS: Stainless steel					

In adhesive tests when considering the numeric results, it's also important to consider the failure mode. When a cohesive split occurs, the test result is the force needed to break apart the adhesive layer. In Table 3, the peel adhesion results of the adhesive formula are generally highest when a cohesive failure mode was observed.

We did notice that the failure mode of the control sample without additional antioxidant was trending more towards a cohesive split of the adhesive. It was considered that elongation of the adhesive increases as the isoprene degrades. Thus we wouldn't expect increasing peel values to indicate effective AO protection. The AO 1400 sample showed 100% adhesive failure mode before and after aging, and lower peel values were obtained.

The Loop Tack test is a quick test involving a light touch over a small test area. The test has a method repeatability of 25%. With this in mind, the loop tack results were all within the same range. The loop tack of the control sample increased after aging, while the three stabilized samples showed comparable tack values after aging. Loop tack values dropped for AO 1010 and AO 1010 FF samples. AO 1400 sample shows better stability before and after aging than the other samples in the loop tack test.

For the static shear test, as expected the control adhesive experienced a large loss of shear strength after aging. We suspect that the rubber's isoprene midblock degradation contributed to this failure. The unaged samples failed adhesively and had ~ 6,000 minutes hang times, but after aging, hang times dropped precipitously and the failures became cohesive. Also, in the static shear test cohesive failure mode observed for all 4 samples after aging. The average hang time increased for the stabilized samples. The initial and aged static shear performance of AO 1400 parallels AO 1010 in this test.

Conclusions

AO 1400 is chemically identical with AO 1010, but with an improved physical form for unobstructed product flow to eliminate bridging during feeding. It is also less dusty and facilitates a more hygienic workplace.

Hot melt adhesive formulations evaluations show AO 1400 provides comparable stabilization performance to the state-of-the-art AO 1010.

Acknowledgements

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