OZONE FOR IMPROVED ADHESION IN EXTRUSION COATING.

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The flexible packaging industry, and in particular the formidable presence of the extrusion coating process in the manufacture of many sophisticated packages, has a vested interest in optimum adhesion being attained between laminates of various substrates. This ozonization up-date will pay particular attention to the improvements obtainable between extrudates and carrier webs on Extrusion Coating lines, by the use of ozone.

KEY WORDS

Extrusion Coating
Adhesion
Extrudate
Ozone
Corona
Melt Temperature
Melt Stability & Neck-In
Odour & Off Taste
Melt Oxidation
Ozonisor
Primers
Ozone Analyzer

INTRODUCTION

In recent years ozone has received a high profile from various government agencies. To some, ozone is viewed purely as a negative by-product of corona treating, potentially exposing us to environmental hazards. Yet to others, ozone has been purposely generated to assist in the extrusion coating process. Before we can explore the advantages ozone offers, we will first look at the history of ozonization, why it was first considered and why increasing numbers of companies are using ozone to benefit their processes.

HISTORY

Ozone as a means of adhesion promotion has been successfully utilized in conjunction with extrusion coating for at least thirty years.

In the first decade of utilization of ozone in the context under review, it was confined to the manufacturing facilities of a world-wide manufacturer of liquid packaging cartons. They pioneered the process, and they remain the largest user of Ozonization equipment.

The dramatic increase in oil prices which took place in the mid to late 1970's and the urgent need to reduce polymer coating weights concentrated minds to seek additional aids for adhesion, and raised interest industry wide, in Ozonization.

Support for the use of ozone from leading polymer producers, including several recently published reports, confirm its importance in achieving adhesion with today's resins and production parameters.

Subsequently, the use of ozone has spread to every continent, wherever extrusion laminators are used to produce flexible packaging, using innovative polymers, requiring enhanced levels of adhesion.

FACTORS AFFECTING ADHESION

Some materials presented to an extrudate, because of their porous nature, will readily accept polymer coatings, but most plastic films and many smooth or glossy grades of paper, do not possess the necessary high surface tension characteristics, to ensure satisfactory adhesion.

This requirement is critical in pursuit of profitable extrusion coating and converting operations and is as much a necessity as the correct melt temperature, die height and nip pressures, in obtaining optimum interply bonding to meet customer specifications.

Factors Affecting Adhesion

* Coating Weight
* Melt Temperature
* Line Speed
* Nip Pressure & Distance
* Polymer Melt Index
* Polymer Density
* Carbonyl Content

Figure 1

The achievement of adequate interface fusion can be particularly difficult where, in addition to adhesion, effective product resistance to aromatic liquids, fruit juices and other penetrative products is required. Line speeds and productivity sometimes have to be compromised in order to eliminate unwanted features such as poor sealing, odour or off-taste, from the finished container.

Since ozone can alleviate some process problems it is necessary to quantify the advantages to be gained by adding ozone to the extrusion coating line, and then look at evidence to show that the benefits can be substantiated. Figure 2

Advantages
1. Opportunity to reduce coating weight
2. Opportunity to reduce melt temperature
3. Enhance adhesion
4. Achieve higher line speeds
5. Optimize melt stability and neck-in
6. Improve heat seal characteristics
7. Reduce odour and off-taste

Figure 2

EFFECTS OF REDUCED COATING WEIGHT

Polymer coating weights which would today be deemed to be high, were always effective as a means to enhance adhesion, as the polymer weight enabled the melt to be nipped into close contact with the fibrous surface, as shown in Figure 3.

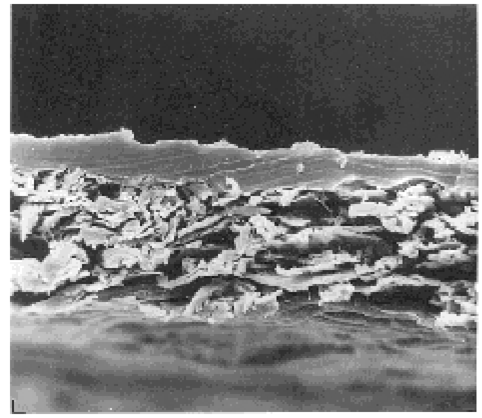


Figure 3

As the coating weights became the focus of attention, following dramatics rises in the price of oil, a desire to lower them developed in all sectors of the extrusion coating industry.

When coating weight is reduced, the actual area of contact between polymer and fibres is minimal because there is insufficient polymer to be nipped into the voids between projecting fibres. Figure 4.

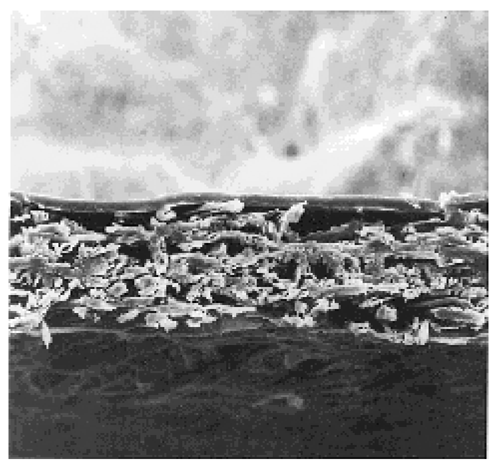


Figure 4

The birds eye view (Figure 5) emphasises the reduced contact when only the gloss surface has actually contacted the nip.

The patches are unsupported polymer sagging over voids in the paper structure.

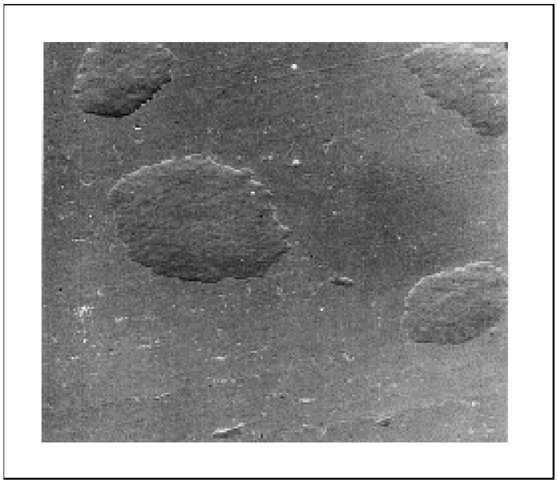


Figure 5

Figure 6 shows in another manner, how higher coating weights will certainly increase adhesion values.

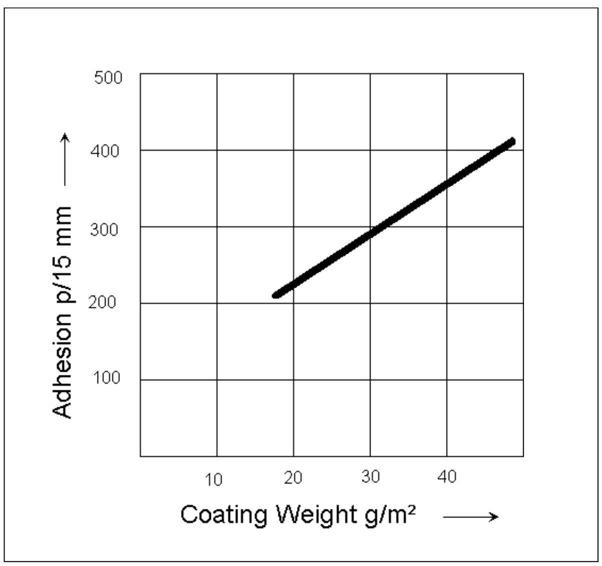


Figure 6
Adhesion of LDPE on Aluminium Foil (using corona at 150m/min - deleting primer results)

REDUCING MELT TEMPERATURE

It is a well known fact that, with a prepared 'smooth' surface, a high temperature melt adheres better than a low temperature melt. With light coating weights this has nothing to do with keying but relates to the level of surface oxidation of the melt, which is accelerated by temperature. The oxidation yields highly polar surface groupings which form strong bonds with the substrate.

Figure 7 shows the contacting surface of an LDPE coating when peeled from the substrate. The coating was applied at a high temperature and a good surface bond to the prepared substrate was achieved, indicated by the delamination of the paper structure rather than clean peeling of the coating. This is due to high melt oxidation.

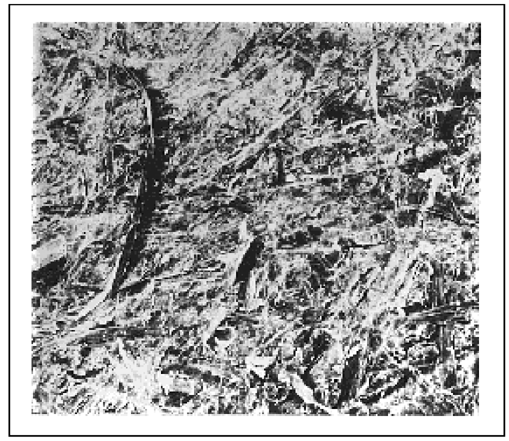


Figure 7
High Temperature extrudate produces good surface to surface bond.

Figure 8 is the same view of a peeled low temperature coating. Note the complete absence of retained paper fibres despite the obvious close contact of polymer and substrate shown by the fibre imprints. The poor bond is due to lack of melt oxidation.

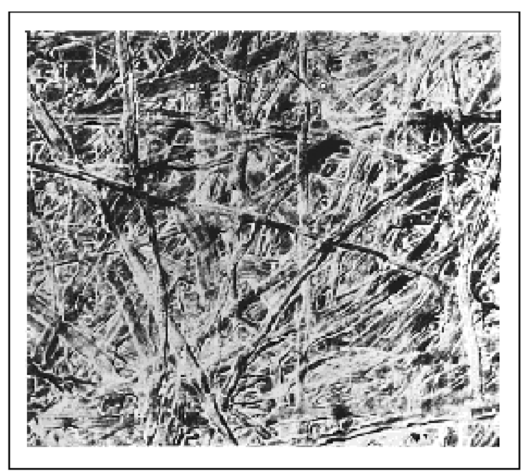


Figure 8
Low Temperature Coating Process Produces Poor Bond

Coatings such as LDPE are non-polar, but the melt will oxidise in the air gap, between the die and nip, to form oxidised, polar functional groups on the melt surface. This induced polarity lead to improved adhesion particularly on non-porous substrates. So enhanced melt oxidisation of the interface surface is essential for good adhesion.

OXIDATION OF LOW TEMPERATURE MELT

Oxidation is a time and temperature dependent chemical reaction. The time is set by the air gap and line speed and the maximum temperature is limited by the product quality requirements, such as odour, off-taste and blocking. Fig. 9 summarizes the effect of specific process conditions on polymer melt oxidation, together with the resultant limitations on the product quality and process optimization.

POLYMER MELT OXIDATION	PROCESS PARAMETER	QUALITY LIMITATIONS
High	Low line speed	Low production rate, high neck-in cooling of melt, odour/off-taste, poor sealing
High	High air gap	High neck-in, cooling of melt, odour/off-taste, melt instability
High	High melt temperature	Odour/off-taste, high neck-in, chill roll sticking, polymer degradation through chain scission and crosslinking.

Figure 9
Oxidation versus process parameters & limitations

The use of an Ozonisor to achieve a rapid preferential oxidation of a low temperature melt enables a good bond to be formed without the problems associated with high temperature oxidation. Ozone is produced under strictly controlled conditions and introduced on to the melt deep in the nip area and only on to the contacting surface, hence the term preferential oxidation.

Ozone is a strong oxidising agent, because the ozone molecule (03) readily decomposes into an oxygen molecule (02) and nascent oxygen (0). The nascent oxygen has a much shorter reaction initiation time and will accelerate melt oxidation. This effect is depicted in Fig.8 where oxygen uptake of molten LDPE is plotted versus time.

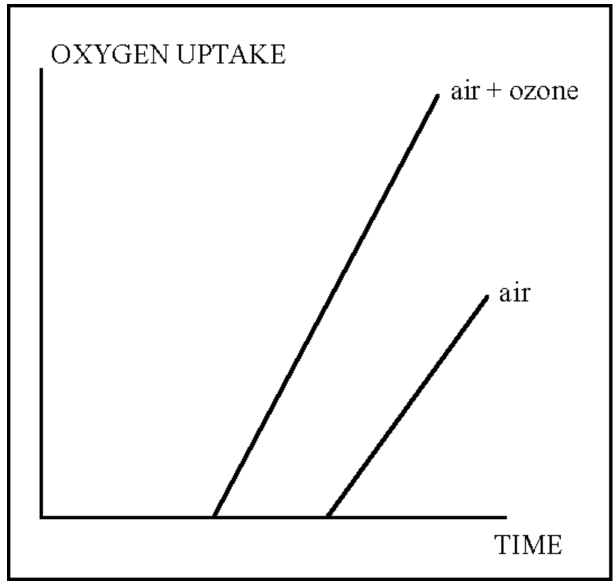


Figure 10 Oxygen uptake versus time

ADHESION AS A FUNCTION OF MELT TEMPERATURE

Melt temperature determines both initiation time and reaction rate. At constant line speed, adhesion is not linearly proportional to temperature, but drops dramatically below a certain critical temperature. This temperature is dependent on the dwell time of the melt in the air gap.

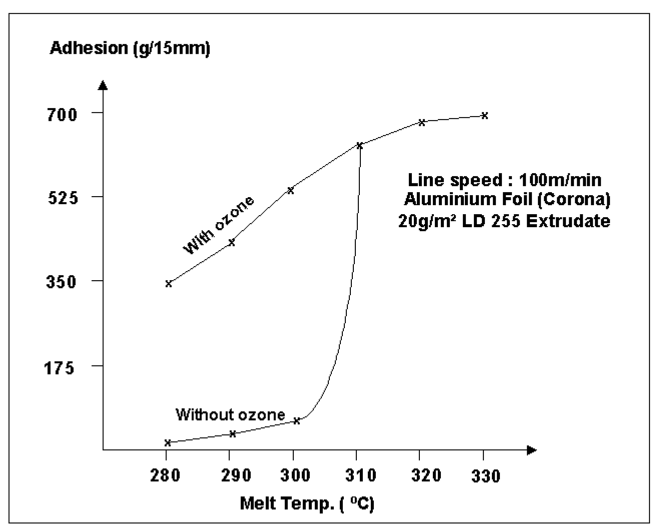


Figure 11
Adhesion as a function of melt temperature

Fig.11 shows that the adhesion is very poor without the Ozonisor, below 310ºC melt temperature. But, by applying ozone, the adhesion value reduces much less sharply.

It can be seen that benefits are available in a reduced dwell time and since the oxidation is preferential, this means that the non-contacting surface will have suffered less natural oxidation. This benefit will also have been greatly emphasised by the reduction in temperature.

Thus, heat sealability will be subject to less compromising conditions.

The same parameters, reduced extrusion temperatures and shorter dwell times, guarantee benefits related to reduced odour and reduced off-taste readings by minimising contact with hot polymer fumes.

EFFECT OF LINE SPEED - NIP DISTANCE ON ADHESION PROPERTIES

The residence time in the air-gap is directly proportional to line speed. With increasing line speed the oxidation will decrease, down to a point where the residence time is shorter than the oxidation initiation time. At that point, oxidation is minimal and adhesion levels will drop. With ozone, the initiation is accelerated, allowing a higher line speed before adhesion deteriorates.

Figure 12 illustrates the adhesion obtainable on kraft paper at respectable line speeds only when ozone is utilized.

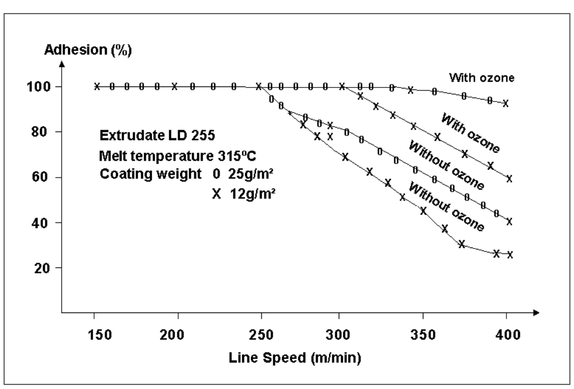


Figure 12
Adhesion on kraft paper as function of line speed

At 350m/min using ozone, adhesion is stated to be 100% and only a marginal decrease in this quality is exhibited at 400m/min.

With LDPE at 315ºC onto matte aluminum foil, it is evident from Figure 13 that acceptable adhesion values with no ozone applied to the LDPE are obtainable only at speeds below 150m/min.

With ozone, adhesion is adequate at speeds some 100m/min higher.

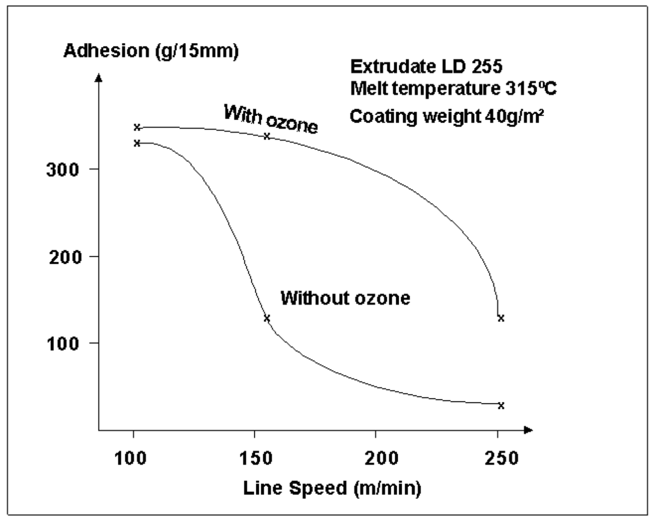


Figure 13
Adhesion on aluminum foil as function of line speed

IS THE SUBSTRATE PRE-TREATER STILL NECESSARY IF OZONE IS USED ON THE EXTRUDATE?

Collating the results of trials run by various organizations, some recent and some over the last ten years, we see the effect the pre-treater, corona flame or primer has on the final adhesion value.

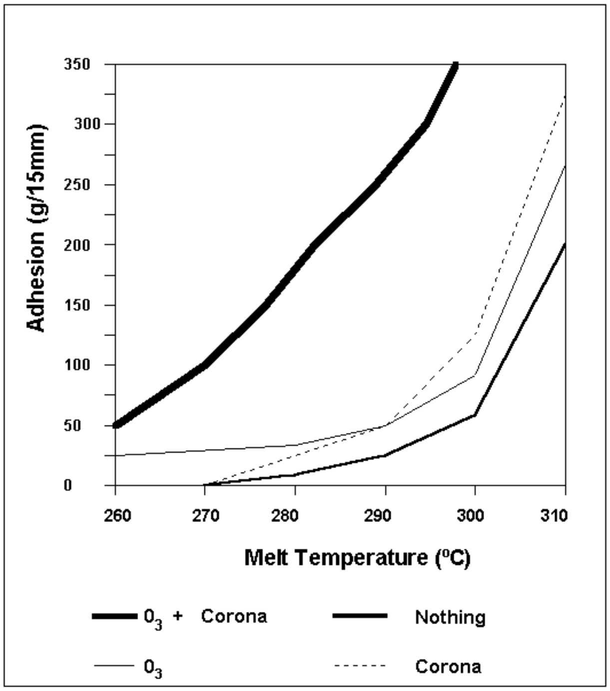


Figure 14 **Comparison of Adhesion**
(PE/MATT Alu Foil at150m/min)

Figure 14 shows adhesion is achievable even without promoters but only with the assistance of melt temperatures above 300ºC.

By adding corona or ozone, adhesion levels are improved even as melt temperatures decrease, but a combination of both corona onto the substrate and ozone to the extrudate, result in very good adhesion even at melt temperatures below 280ºC.

In every test conducted on pilot lines equipped with both corona and ozone generators, it is always established that the use of corona and ozone results in better bonds than is the case when only one form of promotion is utilized. These facts are illustrated in Figure 15.

EXTRUDATE	:	LDPE, 320ºC COATING WEIGHT 25 GSM
SUBSTRATE	:	SOLID BOARD

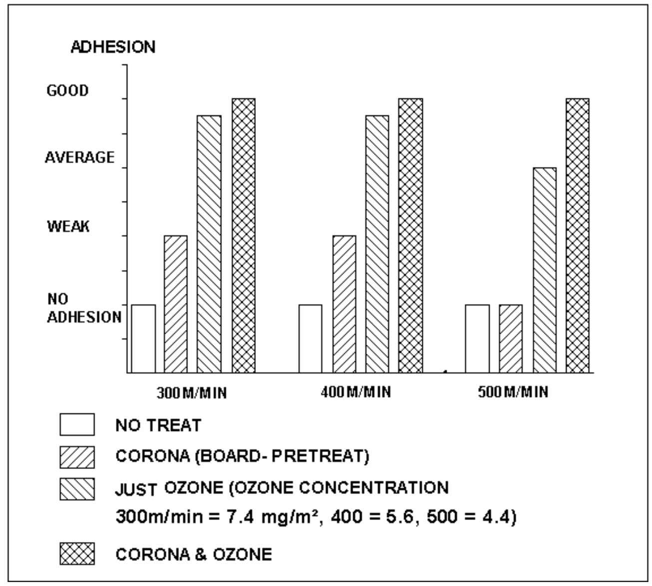


Figure 15
Good Adhesion only when combining corona & ozone

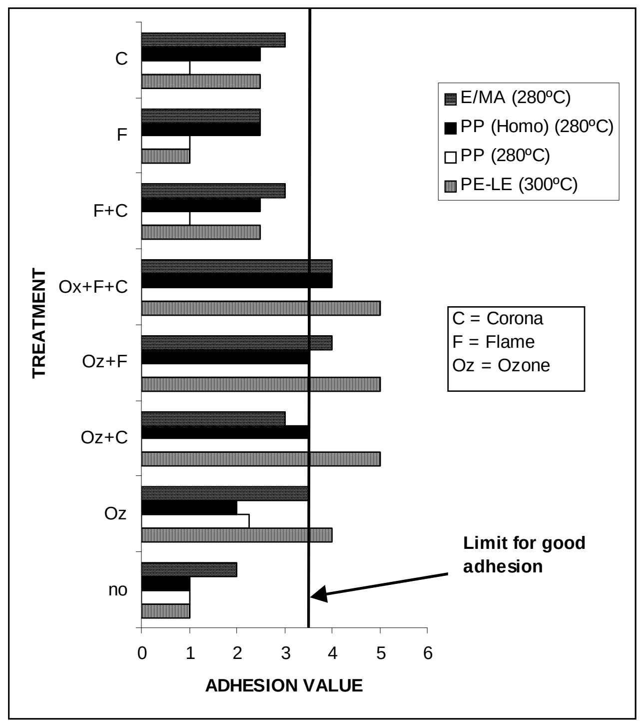


Figure 16
Effect of the pre-treatment on adhesion with different resins

It is clear from these tests the carrier substrate pre-treatment also plays a large part in the adhesion value. Ozone must be used not in isolation but in conjunction with an additional pre-treatment source, corona or flame, both used together seem to offer little further increase in the adhesion value.

ADHESION WITH DIFFERENT SUBSTRATES

Continuing tests involving corona and or ozone on different substrates, such as polyester and nylon, show that optimum adhesion always results from the use of both promoters rather than one. On polyester, less ozone is required to achieve results equal to those obtainable on nylon, when more ozone is required. Figure 17

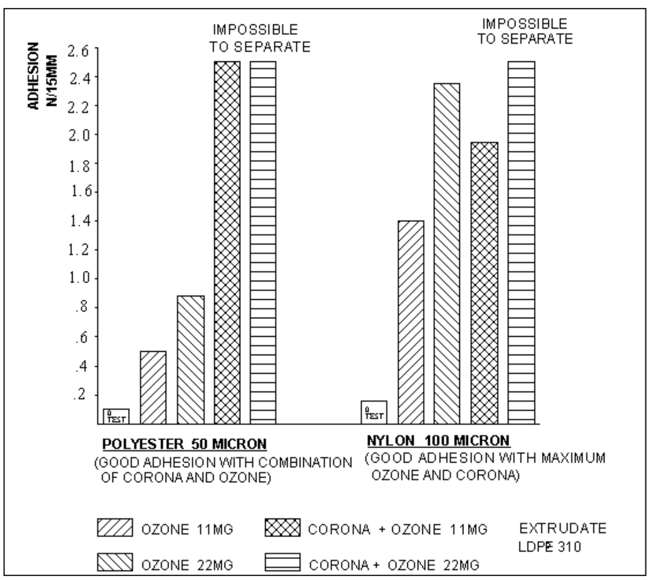


Figure 17
Adhesion with different substrates

ADHESION WITH PRIMERS IN LINE

Some further laboratory and commercially run tests reveal the benefit of ozone when aqueous primers are used on the substrate.

Figure 18 shows that the typical extrusion coating temperature for LDPE was reduced as shown

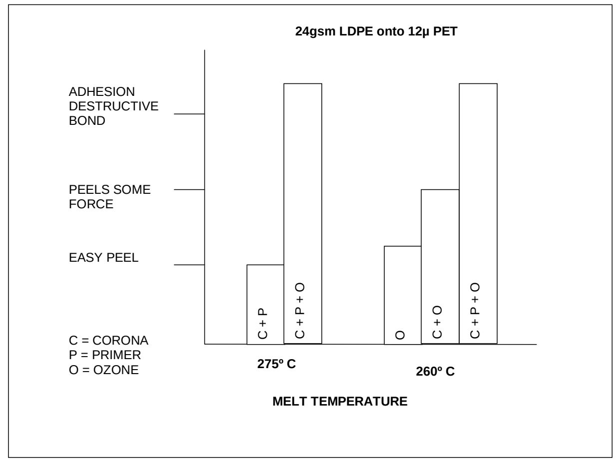


Figure 18

Figure 19 illustrates work based on a commercial process which typically is run at 91 mpm with a 305º - 315ºC melt. Ozone demonstrated the capability of reducing the melt temperature to 288ºC. Addition of the primer to the paper while using ozone, then demonstrated the capability of reducing temperature further to 274ºC and doubling line speed.

Substrate - Solid Bleached Sulfate Board/12 gsm LDPE - Extrudate		
Speeds	Actions	Results
91 mpm	288ºC, Corona, Ozone 274ºC, Corona, Primer, Ozone	Fibre Tear Fibre Tear
182 mpm	274ºC, Corona, Primer 274ºC, Corona, Primer, Ozone	Peels

Figure 19

THE EFFECT OF EXTRUSION TEMPERATURE ON ODOUR AND OFF-TASTE

The organoleptic problems that high melt temperature cause have been known for a long time. When LDPE oxidizes a variety of compounds (aldehydes, ketones, acids) some of which give packaged products foreign tastes or odours, are formed on the surface of the plastic. On the other hand, a certain amount of polar carbonyl groups are needed to ensure adhesion.

To measure these effects in the laboratory aluminum foil was coated with $50g/m_2$ LDPE over a melt temperature range from $245^{o}C$ to $322^{o}C$.

At a line speed of 50m/min and an air gap of 15 cm, odour and off-taste were determined.

ODOUR

It should be noted that in Figure 20 the average score is calculated with 100 being equivalent to zero odour level.

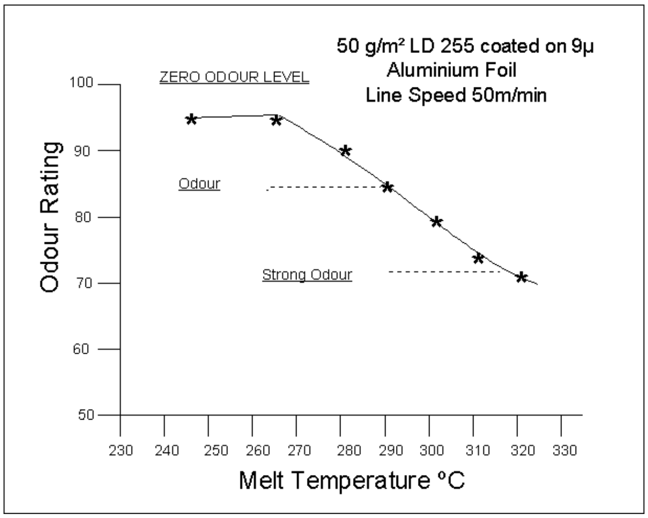


Figure 20
Odour vs extrusion temperature of Escordene LD255

In Figure 20 the deterioration in odour with increase in temperature is demonstrated. The critical temperature is in the region of 285 - 295ºC where the odour level is beginning to move into the "strong" region. Odour level remains constant below 280ºC.

OFF-TASTE

The taint or off-taste imparted to water follows the same trends as illustrated in Figure 20

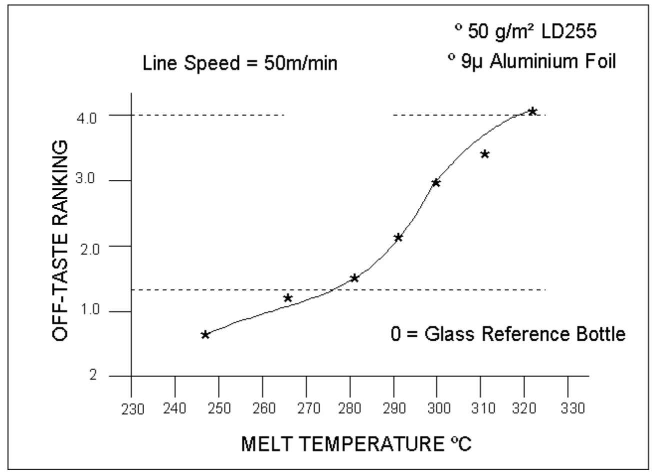


Figure 21
Off-taste vs extrusion temperature of Escordene LD255

At melt temperatures below $280^{o}C$, off-taste rating begins to be indistinguishable from the glass reference. Water is extremely sensitive to tainting, and was for this reason, deliberately selected as reference.

OFF-TASTE REDUCED WHEN OZONE IS APPLIED

Clearly, excessive melt oxidation will lead to the degradation of the polymer, resulting in odour or off-taste within the laminate. This feature is very critical when the finished product is to be used for food type packaging. Fig. 19 shows that equal levels of adhesion at low temperatures are achievable regardless of line speed, but only with the introduction of ozone, to achieve preferential oxidation, will off-taste/odour be significantly reduced.

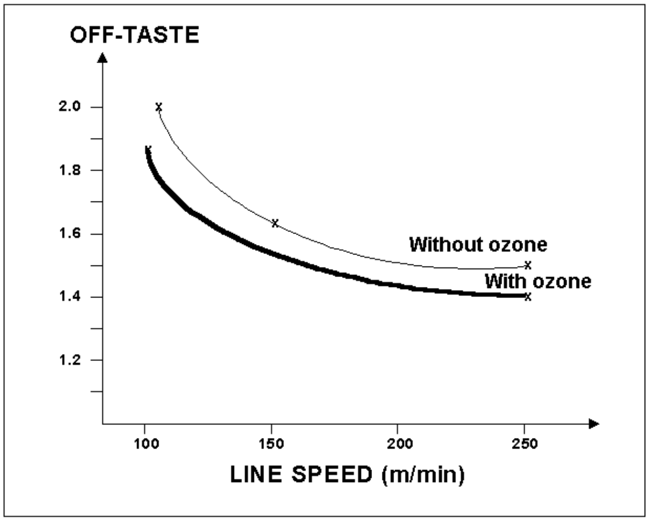


Figure 22
Off-taste as a function of line speed

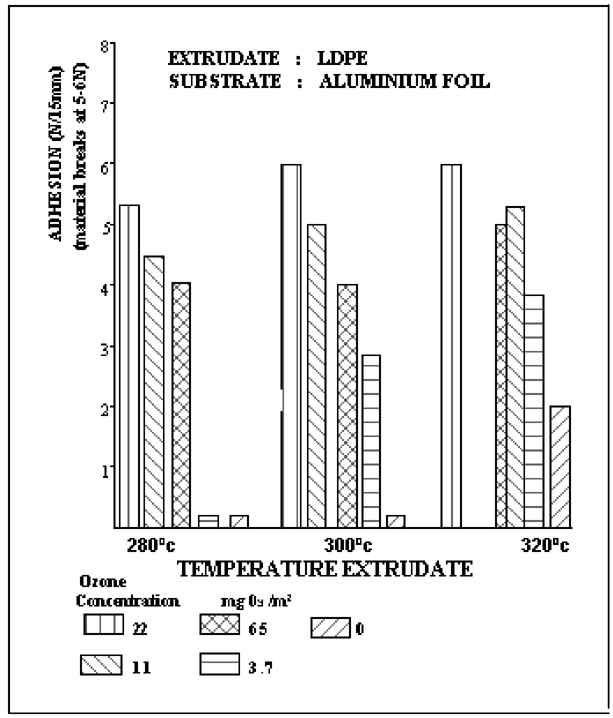


Figure 23
Adhesion against ozone concentration

CONCLUSIONS

Odour and off-taste problems are always a risk when LDPE oxidizes. The risk is not elemental even when low temperature is used.

The interdependence of LDPE tainting of drinking water with extrusion temperature, shows that a critical temperature zone is reached at around 280ºC, above which, odour and off-taste rapidly increases as oxidised by-products from the LDPE are formed.

EFFECT OF OZONE CONCENTRATION

Tests at four different levels of ozone concentration, at three different extrudate temperatures for LDPE onto aluminum foil, shows clearly that more ozone significantly improves adhesion. A 13% reduction in extrudate temperature to 280^{o}C results in only a 10% reduction in adhesion when 11mg of ozone is applied. A doubling of ozone to 22mg/m^2 does not dramatically improve adhesion and confirms that 8-10mg of ozone /m^2 is a satisfactory amount to work with. Figure 23

Ever increasing concentrations do not bring commensurate benefits, as the molten polymer takes time to absorb the ozone and the higher the concentration, the longer will be the time required for absorption.

ON LINE MEASUREMENT OF OZONE CONCENTRATION

Due to the high cost of an Ozone Analyser to measure ozone concentration on-line, these units have not willingly been utilized on many extrusion coating lines, unless located in R&D Centres at polymer manufacturers laboratories.

Today however, with the much greater emphasis placed on customer service and the importance attached to total quality control and repeatability of product specifications, the Ozone Analyser becomes essential as the only reliable tool available, to measure ozone concentration applied to the polymer melt.

The Analyser is located so as to measure the ozone gas stream as it enters the ozone applicator.

The operating principle is by UV absorption with levels of ozone concentration in g/u³, or % weight or % volume.

These values will be displayed on a high resolution flowmeter display.

Programmable alarm settings allow signals to be sent back to the Ozone Generator to trigger, as required, an increase or decrease in the amount of ozone produced in order to maintain the concentration at the level required for repeatability of product.

EFFECT OF OZONE APPLICATOR POSITION

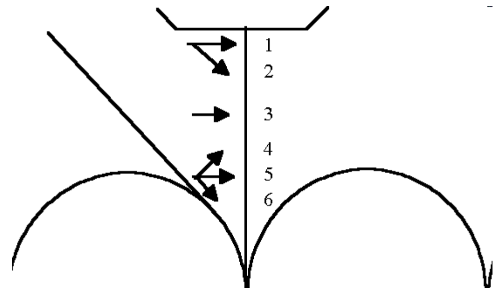
Tests were conducted to evaluate the effect of ozone applicator position, in relation to the melt.

The applicator tested consisted of a tube, with 1mm diameter holes drilled 10mm apart. With a 20cm air gap and all machine parameters constant, the ozone applicator was used in different positions as shown schematically in Fig.24.

In order to obtain significant differences, the following critical conditions were chosen:

*	melt temperature	:	295ºC
*	coating weight	:	20g/m²
*	line speed	:	150m/min

Distance between applicator and melt was 4cm. Adhesion was expressed as a percentage of the highest value.



- position 1: adhesion 66%
- position 2: adhesion 62%
- position 3: adhesion 61%
- position 4: adhesion 88%
- position 5: adhesion 100%
- position 6: adhesion 99%

Figure 24
Applicator Positioning

In position 5, where the highest adhesion level is obtained, the test was repeated with applicator distances from the melt of 2, 4 and 6cm respectively.

*	position 5 - 2cm - adhesion 97.5%
*	position 5 - 4cm - adhesion 100%
*	position 5 - 6cm - adhesion 90%

The results show that ozone must be applied relatively low in the air gap. Since the drawdown ratio can be 100:1, the melt surface will increase in this ratio as it travels through the air gap. Therefore, the ozone applied lower in the nip will react over a bigger surface.

The low position of the applicator into the nip area, and the deckling of the applicator width to suit the extrudate width, ensures that ozone in the surrounding work area will never exceed the accepted maximum level of 0.1ppm.

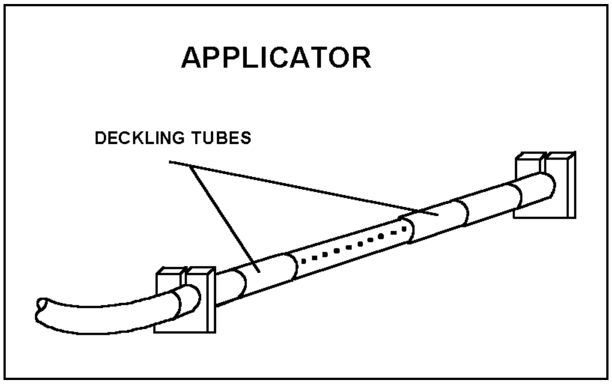


Figure 25
Applicator fitted with deckle sleeves to ensure that ozone is retained within extrudate width

The applicator is designed to suit the nip area and is manufactured from a corrosion resistant material and should meet the following criteria:

* Provide full width ozone application to the extrudate

* Permit deckling to minimum extrudate width

* Ensure constant velocity of applied ozone

* Ensure no disturbance of extrudate polymer melt

A typical layout of the equipment required to achieve a successful use of ozonization equipment, allied with corona treatment is shown in Figure 26

THE OZONISOR - OPERATION & HARDWARE (Figure 26)

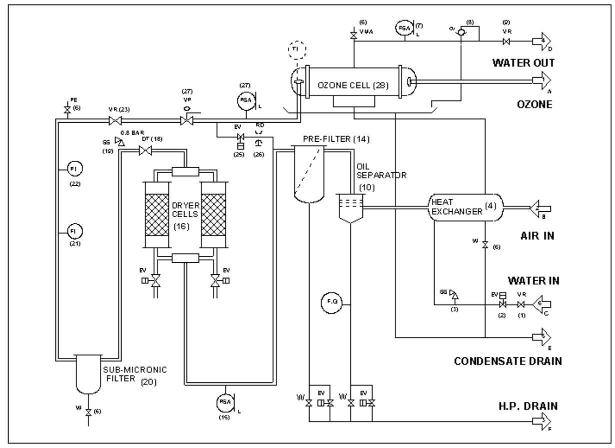


Figure 26
Typical Ozonisor Flow Diagram

Clean, oil free, ambient air at 21ºC is fed into the system at a pressure of 620 KPa and at the design flow rate. The gas passes through a PREFILTER, a COALESCING FILTER and enters the desiccant DRYER where its dewpoint is reduced to at least -51ºC. The dried gas moves to a POSTFILTER and then through an OZONE SHELL. PRESSURE REGULATOR where its pressure is reduced to approximately 55 KPa.

A GAS FLOWMETER measures the rate of clean dry gas going to the OZONE SHELLS. A PRESSURE RELIEF VALVE is located upstream of the GAS FLOWMETER and is set at 83 KPa, the maximum working pressure.

The gas enters the OZONE SHELL(S) where it is exposed to an electric discharge corona which produces ozone from the oxygen present in the gas. The ozonated gas exits the OZONE SHELL(S), flows through a manually operated OZONE OUTLET VALVE and leaves the OZONISOR via the OZONE OUTLET PORT to the OZONE APPLICATOR

CONTROLS AND INDICATORS

The schematic diagram in Fig. 25 is representative of the controls and indicators which are available on all sizes of Ozoniser from 10 gram/hour to 1000 gram/hour. Figure 26 shows a typical 750 gram/hour unit.

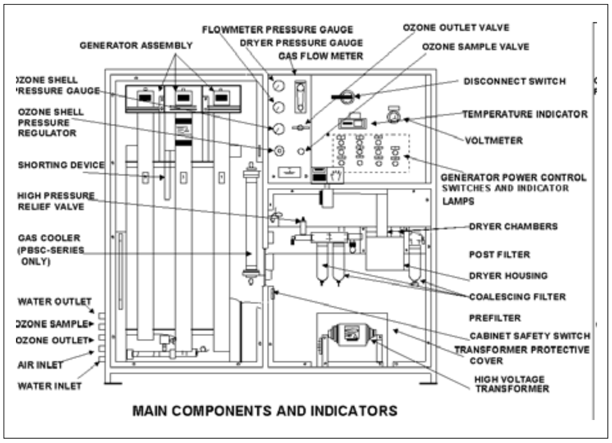


Figure 27
90 Gram/hr Ozonisor Schematic

Ozone output can be automatically controlled from a PC either directly or via a remote control panel on the operator's side of the extrusion line.

Figure 28
120 Gram/hr Ozonisor

TYPICAL AIR DRYING SYSTEM FOR AN OZONE GENERATOR

At any one time, one cylinder is drying the atmospheric air before it is passed to the ozone production chamber, while the second cylinder is being regenerated. Warm air is forced through the dryer, (the direction being opposite to the production flow to ensure that moisture in the alumina is not transferred to the ozonisor elements).

The timing mechanism for the heaters and solenoids (which route the air in the correct direction for either drying or regeneration) are controlled by a series of cam operated micro switches. Thus, if the ozonisor is shut down at any time, the timing cycle will continue in the correct sequence, when production recommences. Although, if there has been a prolonged shut down, one regeneration cycle must be completed before commencing ozone production.

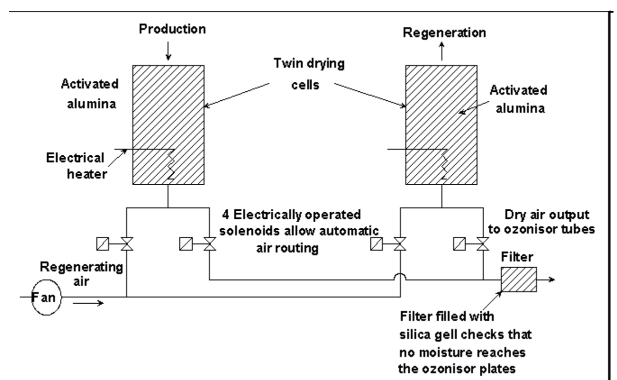


Figure 29
Typical air drying system for an ozone generator

EFFECT OF HEAT ON OZONE OUTPUT

Figure 28 illustrates the mechanical set-up in the ozone creation zone of the ozonisor.

The result of the high voltage discharge in an enclosed chamber structure is the creation of heat, which will be absorbed into the cooling water, in the water jacket surrounding the electrodes.

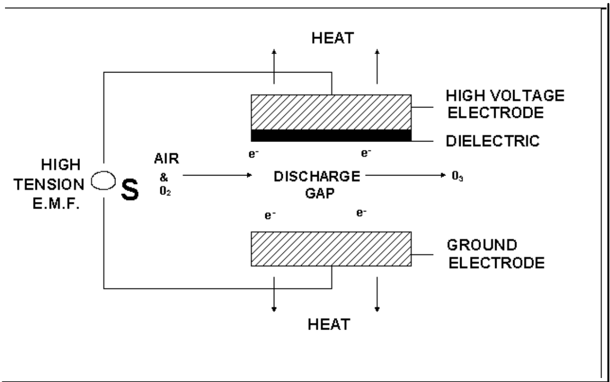


Figure 30
Corona discharge gap

Figure 31 shows the dramatic effect on ozone output in % terms as cooling water increases in temperature. It is therefore imperative to ensure that the water supply to the ozonisor approaches the ozone creation zone at a temperature below 25ºC, so that the effect of absorbing heat from the electrodes is nullified.

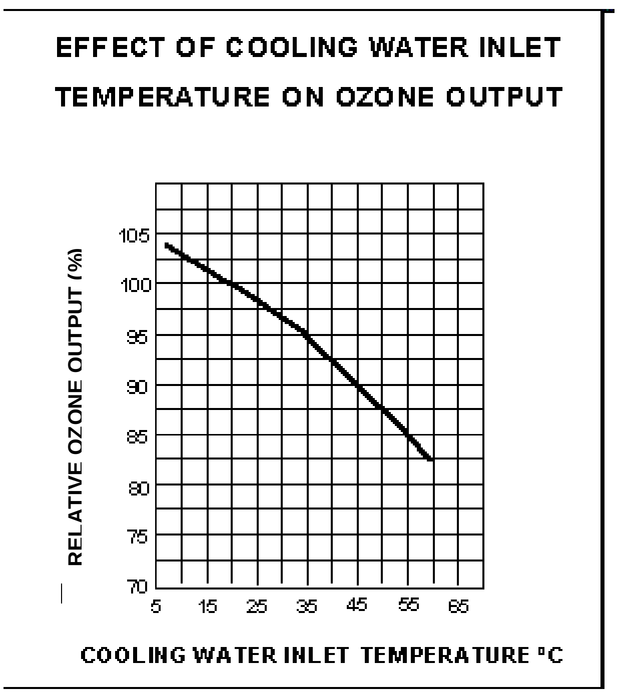


Figure 31
Effect of cooling water inlet temperature on ozone output

SAFETY FEATURES AND CONSIDERATIONS

1. OZONE DESTRUCTION DEVICES

During line stoppages and also at other unexpected times, it is necessary to be in a position to convert the ozone produced from the Generator into a harmless medium.

This requirement is easily met as ozone can be easily and cheaply converted to oxygen by passing it through a suitable catalyst.

A compact ozone destruction unit can therefore be sited at an appropriate location in close proximity to the line so that, as and when required, manufactured ozone is immediately diverted to the destruct unit and rendered harmless.

2. OZONE GENERATORS

The Ozone Generator is a piece of high voltage equipment and is therefore fitted with:

Key operated power supply door switches. Electromagnetic interlocks to all doors and panels. It is supplied with custom designed HT grounding tools.

INDICATORS

Individual indicators show power on, ozone on, air fault, water fault, electrical fault emergency stop; so that all services and conditions are positively monitored.

SEQUENTIAL CONTROLS

Water supply, dryer chambers and ozone production shells each have dedicated flow meters and regulators interlocked, to offer cut-out protection in the event of an overload, underload or pressure loss.

Ozone production is within a sealed circuit and can only emerge at the applicator, with ozone flow being diverted from the applicator to atmosphere or suitable ozone destruct unit during emergency stops and web breaks.

3. THREE WAY DIVERSION VALVES

The safety of personnel demands that Ozonization equipment will always fail safe.

To this end the introduction of a solenoid actuated three way diversion valve into the ozone output pipework ensures that any unpredictable time - for example an emergency stop, or a web break, as well as during start-up, the ozone flow can automatically, and independent of human assistance, be directed from the applicator-operator area, to atmosphere, or to the aforementioned ozone destruction device.

4. START UP PRECAUTIONS

These include the use of Dewpoint testing equipment and the obligatory purging sequence, both contributing to safe and trouble free operation.

OZONE EFFECTIVENESS

When melt temperatures need to be low to obtain benefit, line speeds will be enhanced and adhesion improved by ozone treatment. Figure 32.

In summary, it becomes clear that even with existing adhesion promoters, if melt temperatures are too low or line speeds are too high, unacceptable adhesion results. If melt temperatures are very high, good adhesion is obtainable at most line speeds, without ozone, but negative effects manifest themselves. Reductions in coating weights and melt temperatures result in reduced oxidation of the extrudate in the air gap, only by adding ozone will economic advantages be exploited, allowing wider tolerances in melt temperatures, air gap, line speeds, melt stability and neck-in.

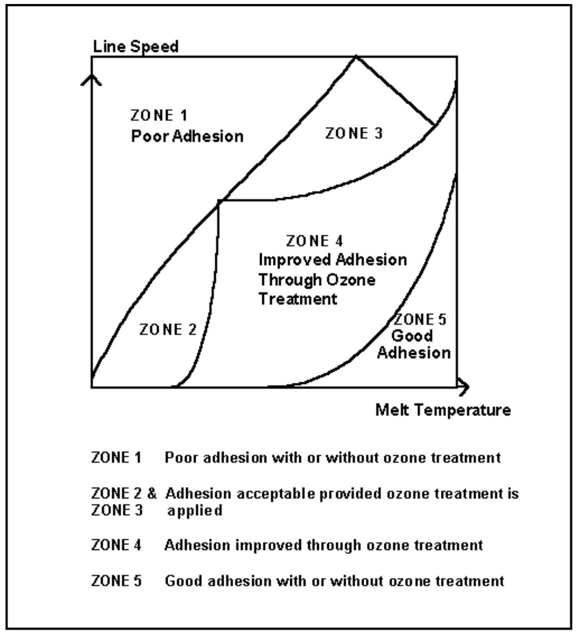


Figure 32
Ozone effectiveness as a function of line speed and melt temperatures

Improved heat seal characteristics clearly are a benefit to be exploited, along with the resultant reduction in odour and off-taste.

Barrier polymers, such as EVAs, which must be extruded at lower temperatures represent polymers whose processing, benefits from the addition of ozone.

ENDS

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