ABSTRACT:

Some basic features are common for all kind of R.A. They are:
Incompatibility with the product to be demoulded both chemical and physical. If moulded material absorbs the release agent, release power is extremely poor and surfacial defects are highly probable.
Lubricating effects to help moulded material flow and moulded item extraction.
R.A. should not be washed off mechanically by moulded material flow.
In the case of die casting a basic property is thermal resistance at high temperature.
Materials technically available in die casting release agents formulation are mineral oils, special silicones, waxes and esters. We need also surfactants because our products are water based.
The job in formulating release agent is mostly empirical and requires a lot of experience. A set of analysis the obtain a coherent picture of thermal resistance of materials commonly used was not exaustive because of the instruments limitations.
Die casting R.A. are water based because the water evaporation heat is very useful to cool down moulds. For this reason are used at high dilution.

KEYWORDS:


INTRODUCTION:

When we make something by moulding normally we need a release agent or a lubricant to extract it from the mould. It is a condition common to almost all type of materials: rubbers, plastics, concrete, metals, baked foods. Die casting release agents are called in foundy world also lubricants because they must have also a very good lubricating power. Are commonly water based and applied at high dilution rates to use the great water evaporation heat to cool the moulds. We do here a short but general overview on these materials.
GENERAL FEATURES

The necessity of using the so called Release Agents when we produce moulded items is a need common to all types of materials like, for instance, rubbers, plastics, building concrete and metals, each one with its peculiar release requirements, easy or difficult to satisfy.

If we consider in general the great world of release agents from the point of view of the intrinsic properties we notice that there are some of them that are common to all kind of products that they must fulfill to reach the target of giving a good release effect.

In other words a good release agent must have the following properties:

- Be inert toward the material to demould. In fact if it is absorbed, it cannot be a good barrier between the mould and the material to demould.
- This condition has another aspect. Being inert means also to avoid any interference, chemical or physical, with the surface of the piece moulded to avoid defects of any kind like porosity, stains, flow marks and others.
- Must adhere to the mould and be resistant to the flow of cast material. If the release agent film is removed, even in a few points, the release is compromised because the moulded piece sticks to the mould and production is slowed or even stopped. Also when it is possible to demould the piece the sticking damages its surface to a certain extent and leads to rejects.
- Must have some lubricating effect and help the cast material flow in the mould.
- Must have lubricating properties to help the piece be extracted easily.
- Must leave no residuals in the mould which are difficult to remove.
- In the die casting field we work at very high temperature. A specific condition is the thermal resistance, good enough to allow the release agent to work well in difficult conditions. I means it should resist at the mould temperature first, to form a film stable enough to survive the time between the application and the metal injection in open air that is an oxidizing situation; then at the aluminium temperature to a certain extent to provide a barrier and lubricating effect.

Lubricating properties are of fundamental importance in die casting field because aluminium is a completely stiff material and does not allow even the small deformations that help demoulding rubbers and plastics. In addition to that, in die casting moulds there are many mobile parts and so called pins that require a good lubrication to work normally. When some of these parts are damaged because of lack of lubrication, the work to repair is very difficult, takes long time and the cost in term of production loss is dramatic. For this reason in the die casting world release agents are more often called “lubricants”.

Everyone today knows that die casting release agents are water based. The active ingredients are emulsified (emulsified itself means emulsified in water). The practice of using water based products comes from a long time ago. Using solvent based products is very dangerous considering the temperature levels common in our field. Solvent based products are dangerous for the health, for the environment, and because of the risk of explosions. But another consideration led to the use of water based release agents: the very high evaporation heat of water is greatly helpful in cooling down the mould. The cooling effect was in the past the only way to control and reduce the mould temperature and is still important today when moulds temperature is commonly thermostatically controlled.

To “put water in” the ingredients which we need to use in our formulations is a difficulty of primary importance for release agents suppliers because to produce emulsions of good quality, stable at the storage under different conditions, and stable also at high dilution degree, requires skilled technicians in laboratory, skilled workers in production and very efficient plants.

Every emulsion becomes unstable when is diluted. The higher the dilution, less is stability.
Another instability factor is the shear effect produced by fast recyclings and strong pumpings, like stroke pumps and these negative conditions have a dramatival influence at the dilution rates encountered in die casting field.

Last condition that makes our work more difficult today is the ecological conscience that reduces the range of products and surfactants readily available to be used without restrictions due to workers health or environment pollution.

PRODUCTS COMMONLY USED IN R.A. MANUFACTURING.

Many years ago, when die casting technology began, the products more often used were heavy mineral oils containing low molecular weight paraffines and polycyclic aromatic compounds, as they came directly out from petroleum first distillation. During the following years due to the technology evolution, heavy oils were abandoned and other materials came into use, such as natural products like refined mineral oils or synthetic. The most important synthetic products was silicones family.

Resinous synthetic polymers have no chances in our field because they do not melt well but remain like semisolid or show a further polymisation; so they make build-up on the mould and are pratically an obstacle to a good lubrication. May be the release itself can be achieved but because of lack of lubricity working with them is impossible.

We can divide the products normally used by Release agents Formulators in five big families.

**Mineral oils**

**Ester oils**

**Siliconic oils**

**Waxes**

**Surfactants**

Mineral oils. Now we use mineral oils more refined than in the past but the content of paraffines and aromatics is still high. Lower is their viscosity and more are refined. Oil classification is based on ISO rules that set a certain number of viscosity levels (at 40°C) as oils official grades.

In our field the most widey used are ranging from 100 Cts grade to 460; 680 is less used today.

Ester oils. Are both natural and synthetic. Natural ones are vegetable oils like soybean, sunflower or castor oils. Synthetic ones are monofunctional esters like fatty acid esters with monooxydrilic alcohols or trifunctional esters of trimethylolpropane. Oleic acid is the most used fatty acid.

Ester oils are widely employed in lubricants formulations but we find them only in few release agents for die casting. The reason may be found in the fact that it is sometimes difficult to emulsify them in the normal way like mineral oils. Other reasons are not disclosed.

Silicone oils. Die casting silicones are called Alkyl aril polysiloxanes. Commonly known as Silicones oils are polydimethyl siloxanes. The general family is the same but the specific properties are very different. Our silicones have better lubricant properties and are easily paintable.

Thermal resistance is very high as every type of silicone.

Waxes. Today the modern technology offers us an interesting family of synthetic products. It is the family of polyethylene waxes. They are widely used because they can substitute mineral oils. Are used grades with a melting point of 100°C and when are molten their viscosity is very low. At high temperatures they behave like oils but do not contain harmful substances. Negative point is that such as
materials solidify on the cold parts of moulds and can create a hard build-up.

Surfactants. Are necessary to emulsify the active ingredients. They are the bond between water and oils or waxes. The quality and the stability of emulsions depend as first instance on surfactants choice. It is very difficult to schematize them because the surfactants world is extremely wide and complex. Roughly we divide them into three wide families.

Non ionic surfactants. Are the most commonly used because their versatility and efficacity is very high. Negative point is their low biodegradability and their degradation is achieved only with very efficient plants of water treatment.

Anionic surfactants. Are less but still used, because they are more biodegradable. Are less versatile than nonionic ones and are greatly sensitive toward pH variations and water hardness.

Cationic surfactants. Are not used because they have poor efficiency and because cationic emulsions are acidic. Corrosion could easily happen in acid media; cationic emulsions are not used at all in our field.

In which way we choose the ingredients for our formulations and how do we evaluate their influence on the overall performance of a release agent? It is an embarrassing question and responding to it seriously is quite impossible because we do not know what happens in the mould but we can only suppose it. We do not know which are the situations that a release agent film is exposed at, point by point, because we do not have analytical devices that can tell us what we need in the real situation. In die casting injection times are milliseconds; No one analytical device can measure temperature rises, thermal exchange, viscosity drop happening in few millisecond.

We do not know what happens to aluminium also in the mould during this short time; we make computer simulations but not measures.

A release agent technician has only four tools. A generic knowledge of materials properties, his fantasy, intuition and experience. He can only extrapolate a behaviour of a certain material at supposed working conditions.

Our job is based on practical tests in production where we compare situations and performances and try to understand which are the focal points that make difference. We suppose a certain behaviour and if it happens we believe to have been right, if not we exclude it, with the complication that results are often apparently contradictory.

In conclusion making release agents, of any kind and for any application, is only empirism with all the negative inconveniences arising from that. We must admit we are not still at a sufficient level of scientifical objectivity.

To begin to overcome the darkness of empirism, few years ago we decided to do a first screening of thermal properties of most common used materials in our field with the ambitious objective of reaching a still simple but coherent picture of the parameters that are the base of release agent performance.

This first tests run had the scope of let us face the problems and difficulties of such an analysis on the point of view of methods validity and equipment possibilities.

We set arbitrarely the mould temperature at 280°C as hottest mould point, like injection channel, and the interface mould/aluminium at 500°C, and we evaluated the weight loss in isothermal mode in an interval of two minutes.

In the following table we list also in third column the time elapsed before the total degradation at 500°C took place. This time was not given by instrument but extrapolated graphically and is not absolutely reliable but only indicative.
This first set of data is not really comparable with what we see in our experience because some of them require to be confirmed or further investigated. There are also some question that need to be discussed in terms of method reliability and results interpretation. Anyway we could formulate two hypotesis and some other comment. First one brings light on the traditional use of silicone and helps explain why it is so important in keeping moulds and pieces clean. Because it is not completely burned at 500°C but is still liquid in a certain amount, the oil makes small graphite particles, coming from oil and waxes degradation, becoming mobile and float away at every demoulding. In this way deposit build up is avoided. This fact seems confirmed if we consider that silicones themselves are very poor in terms of release power in our field, unlikely in other fields like rubber and plastics. Graphite removal leaves the mould without...
the protective and releasing layer that is one of the mechanism commonly accepted to explain how a release agent works in die casting field. The experience confirm that large excess of silicone in formulation are rather negative than useful.

Second one is the wax degradation at 280°C higher than mineral oils do. Both products family are hydrocarbon but waxes have a higher molecular weight and for this reason should fragment by thermal decomposition in bigger parts less volatile than oils. We should confirm the data first, then investigate and try to find an explanation on the chemical point of view. But on the other hand, we could confirm what the experience tells us: release agents with high quantity of waxes form higher graphite quantity than oil based ones; moulds are dirty but when are old and damaged the thick graphite layer covers very well all surface defects. Also residuals at 500°C, if confirmed of course, could be explained as graphite residuals.

Esters are quite good at 280°C, except Butyl stearate of course because it is a little molecular weight, but at 500°C seems far worse than mineral oils and undergoes a faster degradation. Could these data explain why esters and vegetable oils did not become popular in die casting application?

The conceptual limit of our first tests is the fact that we decided to observe materials thermal degradations in a fixed time of two minutes. Thermal analysis equipments are very precise but are not very fast. For such a reason we hoped to reach precision and reliability and we did not imagine the data flatness we got. It was a “testing test”.

Another negative point was the fact that we made our tests using an external laboratory. We are not equipped to do by ourselves thermal analysis and we could not, for economical reasons, repeat tests many times to clarify the doubts as we could have done if we would own our instrument. Two minutes are an enormous interval related to injection times. Contact time between liquid, metal and release agent film is very short and also when aluminium solidification begins, its adhesion on the mould is no longer possible. What will happens to release agent film at this point is of secondary importance for releasing but is fundamental for mould cleanliness and the aesthetics of pieces.

It should be necessary to understand what happens to release agent film during the short injection time to define the properties that govern release and during the longer time between injection and extraction for dirty build up both on moulds and mouldings.

To understand what happens to our lubricant film simply means to know the temperature – time relationship at the film – aluminium interface. That comes first. The second point is to have reliable data on thermal stability of our materials. If it is impossible, as seems, to make direct measurements it should be possible to extrapolate the initial behaviour with a good probability of being right.

When we will know the temperature evolution and thermal stability we will then have the possibility to predict with sufficient accuracy the overall performance of our release agents.

In our first tests it was impossible to deduce with enough precision a behaviour just after starting the analysis because the instrument stabilisation altered significantly every initial value.

Modifications in chemical structure both by oxidation and by thermal degradation could be the explanation of a property that we have mentioned before. One general property of every release agent is the mechanical film stability. It must not be washed off by injected material flow.

In other application we reach the scope by increasing the viscosity but at high temperatures as we encounter in die casting, waxes and oils viscosity drops down to a negligible value. But just after application oxidation of our film begins taking place. Oxidation means polar group formation that are responsible for the strong adhesion of film itself on the mould, necessary to withstand abrasion associated with flow. The influence of polar groups as adhesion points is well known and products with strong polar groups are widely used in high technology fields as adhesion promoters for a better bonding of different materials.
RELEASE AGENT APPLICATION

Die casting release agents are not used as supplied but are diluted with water, of course, at a ratio ranging from 1% up to 4%, mostly from 1% to 3%, of product as received and applied with automatic dispensers. Only few customers still apply it manually.

Automatic dispensers are of three types. Based on vertical sliding with multiple nozzles that “wash” the mould; with vertical sliding again but with oriented nozzles to spray better where necessary to apply more lubricant; with multiple axes robots. First two are the most popular because they are less expensive than anthropomorphic robots. But dispensers with oriented nozzles or robot assisted are used on well thermoset moulds because they apply less release agent than the first one and do reduce less the mould overtemperature.

Material dilution with water can be done manually or with metering units, machine by machine or in a centralized tank. It is obvious that the best condition on the technical point of view is achieved by using an automatic metering device for each machine. In this way we could use different types of release agent specific for each situation with a great technical benefit and cost saving.

Talking about application we should remember the physical phenomena we see when we spray a liquid onto a hot surface. Vapour layer formed first, insulates the liquid drops and rebounds it. It can be an obstacle against a good film formation but I do not think it happens in our field because we force the contact by spraying at high pressure. But we should consider, instead, the negative possibility that spraying at high pressure, the flow can wash off the release agent already deposited. If the water evaporation is discontinuous because of big vapour bubbles and spurts, the release film is discontinuous too. Spraying conditions must be deeply investigated to establish the relationship between spraying pressure, applied quantity, atomisation and other parameters. Some research group is already involved in this question; researchers of University of Brescia have already issued papers on this matter.

We should consider and discuss now another important point to complete our overview on release agents for die casting. It is the property of cooling down the moulds that lubricants have. Many technicians are convinced that products have not the same moulding cooling power. Normally it is only a feeling they have and I would be sceptic about cooling differences but I remember that an important customer told me that they recover different quantity of diluted lubricant after spraying when they use different products. Such a difference means a different quantity evaporated and consequently different final effect over moulds temperature.

It is something existing really and could we accept it to confirm a different cooling power or try to find some other explanation? In every factory, in production, there are so many things to follow and many problems to solve every instant that technicians have no time to investigate and explain what is not immediately necessary. May be the reason for this difference is another.

If we consider that every customer is using the concentrated lubricant diluted at very low rates, it means that they spray water with 1 or 2 percent of lubricant. Similar difference on water purity is absolutely negligible in terms of cooling power. Evaporation heats differ so little from pure water one and commercial product by product, that every other variation in machine conditions like ambient or aluminium temperature or machine stops for normal little inconveniences have a bigger influence on moulds temperature. In other words, if concentrated release agents may have different cooling power because of different formulation at such as dilution rates every difference in terms of evaporation heat is not to be considered.

A parameter we may consider in such as situation is diluted lubricant surface tension because it can be also influenced by a very little amount of surface active additives. I made some test to clarify the influence of different surface tension values but I could not see any effect of any kind against the
release agent normally supplied. Surface tension is important to reach a good atomisation when we spray in a proper way a small quantity of product to atomise it in very little droplets. When we spray at high pressure a large quantity as we do in our field we do not atomise the product in fine particles but we make a continous jet. Surface tension has no influence at all and could not help us. Another possibility is that the surface tension of release film already deposed on the mould plays a certain role; but it can be possible only if there are normal silicones in the formula that repell water and are not destroyed completely at the temperatures we encounter in die casting. But in this case the release is compromised because the film formation is insufficient; if the small quantity can of real influence.

Discussion on cooling properties is still open only because the afore mentioned customer found certain differences between the products he was using. In my opinion the probability that we can find any difference between commercial product is extremely little.

ACTUAL SITUATION

Lubricant based on heavy mineral oils are of little interest now. Only few traditional commercial products survive but are less used day by day. Heavy oils with a very high thermal resistance were necessary long time ago when pieces were thick and their exotermicity high but today the moulding technology has reached a good level and we produce pieces with very narrow thickness with low exotermicity and with complicated shapes. Narrow thickness and complicated shapes lead to complicated aluminium flow in the mould with a strong mechanical washing on lubricant film. Only synthetic materials can be used with success in difficult situations because low quality levels of moulded items are not longer accepted. Mechanical strength, uniform internal stucture and surface quality are conditions imposed today to our field. Old type lubricants produce a lot of graphite and scorched material build up entrapping a lot of gaseous microbubbles; they can have, to a certain extent, the same effect as activated carbons. The greater consequence is the possibility of porosity into the metal directly by gas diffusion or because the carbonised layer slows the metal flow, produces microvortexes and some air can be encapsulated.

Synthetic materials, mainly based on silicone, help liquid metals to flow and hold little gases. Silicones remain liquid and, have some lubricating effect and the portion destroyed at the injection conditions produces silica particles without the carbon typical porosity. It is obvious that a good flow means also better structure uniformity.

Another point I feel necessary to mention. It is the aesthetic exasperation required also in die casting field in same way like in other fields. Technicians do not only ask for materials with a good technical quality but are also seeking for aesthetic quality of pieces; moulded items must be absolutely clean and bright; suppliers very often make their battle on pieces surface aspect. This exasperation, that we can define as virtuosism, is the visible part of good moulding ability; it is the way to show it at sight.

FUTURE TRENDS

We said above that the job of release agent technician is empirical. The hope for the future is to know with sufficient precision the liquid metal flow so that we can see point by point what is the local temperature and heat exchange ratio to see the thermal stability required. It is also necessary to know the local pressure on mould walls to establish the resistance to the washing necessary for a specified geometry. Of course thermal resistance and flow resistance are not independent but must be considered as two faces of the same problem. We must know what happens in the very short time during the
injection. Maybe the level of precision and reliability of computer simulations of moulding parameters could be already sufficient to give the information we need, or will be sufficient in a short time. But if that is also true, another point remains set in stone. This point is the knowledge of thermal behaviour of materials available for our purposes with the sufficient precision and reliability. Without it we always remain in the same empirism as before and today. Today we can obtain data on thermal stability of all materials with the existing equipments but these data are not referred to the real injection conditions; if we do not know exactly but continue to imagine and suppose and compare, we remain in the same empirism. Efforts must be done to bring light on first instants. Release agents become important only when for some instance there is a problem and they do not work well and all the production stops. When everything is running normally, these materials are put in a corner. But they represent the base, the starting point of production possibility: to extract from the mould what we produce. Without them it is not possible to make moulded items. It is very strange that an entire world, the die casting world, is based on the sole empirism and up to today no researches are made by scientifical groups to clarify the focal parameters that govern the matter. It is not easy but is necessary; the progress comes from knowledge.

REFERENCES

1) G. RAMPI, Diecasting Technology. Edimet ( December 2001 ) p. 51
2) G. RAMPI, Diecasting Technology. Edimet ( December 2002 ) p. 49
3) A. PANVINI, A. POLA, Diecasting Technology ( June 2001 ) p. 32