Functional Additives for the Plastics Industry

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A Report from Rapra's Industry Analysis Group

by

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RAPRA INDUSTRY ANALYSIS

Technology and Markets in Context

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If you feel that these are areas in which your company would benefit from some expert assistance then telephone us right away on +44 (0) 1939 250383, or fax us on +44 (0) 1939 251118, to discuss the matter further or to arrange a convenient appointment.

Rapra Industry Analysis - Consultancy Services for the Polymer Industry

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1. INTRODUCTION

1.1 Background

Functional additives are an essential and often expensive part of many polymer formulations - used both to ensure the efficient processing of materials and to enhance the properties of the finished product in some way. Protection against degradants can be provided as well as the means to produce lighter, foamed products or tough flexible ones. Colourants and fillers are also components of a finished artefact which come in a variety of guides to provide the best solutions of a particular customers' requirements.

These applications are governed not only by the polymer systems but also by factors such as legislation, consumer pressure, environmental factors and technical developments. Conversely, the markets for additives are strongly related to those for the polymers in which they are used.

Additive suppliers are constantly developing new products in response to technological needs within polymer applications and to satisfy ever-increasing environmental requirements and health and safety standards. A variety of the functional additives currently used in plastics are the subject of environmental concerns e.g. the use of heavy metals in stabilisers and pigments. In addition, health and safety concerns over dust are driving the increased use of additive concentrates or masterbatches.

A review of this field was compiled and published by Rapra in September 1994 which has since been in steady demand. We felt that sufficient had happened in the additives sector both technologically and in business trends for the time to be ripe for a new edition.

It is still an area of growing importance and change for the both the polymer industry and additive suppliers. The current review has revisited the marketplace and reports on those changes and trends to bring the reader new information in the same style as before.

1.2 The Report

The report starts with an executive summary in Chapter 2 and is followed by a discussion of the different families of additive materials and their major uses in Chapter 3.

Chapter 4 covers recent product development and general applications, which can be read alongside such information in the previous 1994 edition.

Chapter 5 reviews the suppliers of additives and the change in consumption of the materials by the resin suppliers, polymer compounders and converters.

Chapter 6 covers developments in resins and polymer markets which impinge on the uses of additives and Chapter 7 discusses points on legislation which are relevant to a range of additives.

Appendices list suppliers of additives and a quick reference to their products, taken from the annual "European Plastics Directory" published by Rapra Technology.

1.3 Methodology

Substantial desk research has been carried out on the various elements of the subject of additives and polymeric materials presented in this report. Use has been made of data gathered in other recent Industry Analysis documents.

1.4 Future Studies

As a follow up to this current report, it is anticipated that Rapra's Industry Analysis Group will be examining further aspects of additives and their role in polymers. These are likely to take the form of a more in-depth look at some of the individual additive families and in addition reviews of plastics compounding activities are likely to be forthcoming.

2. SUMMARY AND CONCLUSIONS

2.1 General

The plastics industry has experienced a return to growth which is several points above GDP figures for Western Europe in the last couple of years. This has renewed the challenge for the supply of high quality, cost effective additives to ensure that plastics compounds can be processed ever more efficiently and perform to higher and wider specifications than ever before. The demand for plastics to function in wider or more "extreme" markets and under stricter regulatory regimes stimulates additive activity.

The re-working of long-standing and traditional workhorse grades of some classes of additive into more environmentally acceptable forms is continuing. Powder versions of old lines are being displaced by uniform pellets or pastilles which release less dust, flow more easily and so allow for greater accuracy in dosing than the older systems.

Another trend seen in recent times is that toward one-pack systems. Plastics often are compounded with several process and other additives, and we now see more commonly the combination of a stabiliser with a lubricant, and other additives where appropriate, in a low- or non-dusting product. The move to multi-component packages of processing aids which takes away the risk of operator error, aids quality control, ISO protocols and good housekeeping.

The main beneficiaries are the PP, PE, PS, and ABS processor sectors where there is a concomitant reduction in the need for on-site capital equipment.

On the environmental front, the effect of results from various studies which have queried the safety of some additives, or their precursors, are not having any great impact, but some doubt is being expressed within the industry over the long-term viability of some classes of product. This has been happening with some flame retardants, plasticisers and heat stabilisers, as well as inorganic pigments. There are no bans on the materials nor hard scientific reasons to do so, but some major companies are taking a keen commercial look. In some cases development programmes for alternatives are seen as the cheaper option rather than interminable "fighting for the truth".

There has been much commercial activity in the last couple of years, with well established additive and fine chemicals divisions of major chemical groups changing hands and new alliances created.

Competition and price pressures have been intensified by new capacity installed to attract business for industry "work horses" after key patents have expired.

As a diverse group of materials there have not been many published figures on consumption of additives.

World consumption for the additives discussed in this book, less fillers, is around 12 million tonnes. In Western Europe the figure is around 2.5 million tonnes with Asia taking about 40%. Growth is overall between 3% and 6%.

All in all, a growing and vibrant market exists for additives and colourants for the world's polymer processing industry.

2.2 Individual Additives

1) Antimicrobials

Orientation for these materials has turned towards the polyolefins as the beneficiaries of new development rather than the traditional sectors of flexible polyurethanes and polyvinyl chlorides.

Market pull rather than technology push has energised this sector as fears, real or imaginary, of illness coupled with the demand for tighter hygiene has driven the demand for plastics housewares with "in-built" protection. European markets are growing for innovative offerings which started in the U.S..

2) Antioxidants

Alongside the development of new compounds, efforts are being concentrated on marketing ready-to-use stabiliser blends or blends of stabilisers with other additives. Special importance has been placed on the development of easily metered, non-dusting product forms.

Other major trends are the increase in Vitamin E consumption, boosted, no doubt, by the ability to claim similarity to the natural materials found beneficial in the human foodchain.

Increasing use of hindered amine light stabilisers as antioxidants in a range of polymers is expected now that their use over a credible temperature range has been verified. Enhanced thermal stability is required from all families of materials as they are called upon to perform at ever higher processing conditions.

3) Antistatic agents

Current antistatic agents will continue to be those most widely employed in the immediate future. New product developments will be less important than the improvement of existing, highly efficient products. Multi functional materials which act as lubricants and dispersion aids continue to be explored.

The highly efficient ethoxylated alkylamine antistatic agents are much improved when used synergistically with other agents. Improvements in the handleability of alkylsulphonates have been achieved.

Amide-based antistatic agents are being developed into amine-free products which can be more freely used in electronics applications.

Intrinsically conductive polymers remain a goal for many, with the first commercial product now available.

4) Blowing agents

In chemical blowing, endothermic types are increasingly finding favour as are blends of endo- and exo- types to match the moulding or extrusion requirements.

Much work continues as candidates for the third generation of halogenated products, HFCs, are brought towards the market and the relevant approvals are sought in the race to meet the

regulatory timetable. Meanwhile, for various products, renewed interest in carbon dioxide systems has prompted research programmes also.

5) Curing agents

Developments for urethane systems continue to be devoted to efficient methods of accommodating the change to the next generation of blowing agents with zero or very low ozone depletion potentials.

There is increased demand for reduced odour and reduced volatility to combat the fogging issue among others, and attention is being paid to the level of catalysts left as residues in finished products.

6) Compatibilisers

Growth for coupling agents continues to be stimulated by the increase in demand for mineral filled polyolefins and in glass reinforced materials.

Pre-treated fillers and reinforcement are the preferred form for efficiency, handling and the minimisation of any health and safety issues.

The processing of mixed waste recyclate has not progressed as thought likely and so demand for polymeric compatibiliser materials such as modified polyolefins and block co-polymers has not yet increased to any significant level.

The development of blend and alloy technology should also provide a market for such materials.

7) Heat stabilisers

After extensive replacement of cadmium stabilisers in Europe, Northern America and specific Asian countries, a substitution for lead-based stabilisers is being made in the medium term and in particular application sectors.

There are no bans on lead products and a more general realisation exists that the relevant products are chemical compounds with the lead in a "bound" form and so far less problematical than other species. Nevertheless, companies are beginning to emphasise their calcium/ zinc and other "non-lead" offerings as choices for an ever wider portfolio of applications.

The rate at which these alternative systems will be introduced is likely to be determined by their success in the particular applications including cost/efficiency considerations.

Tin containing stabiliser products are not likely to be among the beneficiaries of the slow move from lead within Europe.

8) Lubricants

There are no significant or fundamental changes in the chemistry of the product types on offer.

Application areas are encompassing filled and reinforced thermoplastics to balance the viscosity changes wrought by the latter's' incorporation into a compound formulation, although the PVC sector remains by far the largest market segment.

The future of lubricants as a product group primarily depends on innovations within plastics production and plastics processing. New materials are mainly optimised with respect to their mechanical properties and material costs as solutions to processing problems.

Potential interaction with other ingredients of a formulation are under continual review to avoid any adverse combinations.

Silicone and fluorocarbon based materials are increasingly considered as processing aids.

9) UV stabilisers

The development of light stabilisers of the HALS type made outdoor use of polypropylene possible for the first time and thereby dramatically increased their application and consumption.

HALS products have found wide application in agricultural films over the last few years.

Handling of light stabilisers has been made considerably easier by the development of non-dusting, granular product forms.

Low volatility for benzotriazoles and good stability are the outcome of current developments but most effort continues to be based on the improvement of hindered amine systems.

10) Plasticisers

The major phthalates continue to be the preferred plasticisers for many applications, despite concerns about volatility, migration and, in more recent times, for their alleged biochemical effects.

When accurately analysed and interpreted, the quantities of phthalates likely to be ingested from toys etc. have been shown to be much less than the levels deemed acceptable by Food and Health authorities for the *daily* intake of these substances from food. They are also easily biodegradable within soil and aqueous media with no indicated harm to aquatic life.

These materials retain around 90% of the market, although the historically high share of DEHP has been slowly declining, despite volume increases, in favour of the higher phthalates.

11) Fillers

Fillers are becoming increasingly important with their annual growth rates often higher than that of some of the fastest-growing plastics. Because of the many extremely effective, functional fillers available and the possibilities for modification by additives and blending; cheaper, commodity resin based compounds continue to challenge for applications where engineering and performance plastics may be seen as "over-engineered".

However, there will always be a large market where fillers are used simply to decrease the price of compounds.

To meet the ever more demanding requirements of the market, the trend is towards finer-particle and in some cases surface-treated fillers. Customised filler mixtures are increasingly being supplied.

To facilitate handling, especially of fine products, use is made of compacted fillers, filler concentrates in granule form or masterbatches.

Talc and calcium carbonate continue to be the most widely used mineral fillers; calcium carbonates represent over 75% of total filler demand.

12) Colourants

Colourants for plastics represent a large sector of industrial activity. The range of various chemical classes of inorganic and organic pigments as well as that of dyestuffs and speciality colourants has been tremendously extended by the various manufacturers.

Although few new classes of colourants have appeared on the market during the last few years, the partial replacement of cadmium, lead and diaryl pigments has been considerably stirring the development work. On the other hand, the production of some colourants has been ceased on either environmental or simply economical grounds.

Colourant preparations for use in commodity polymers must be dust-free and easy to process. These requirements have led to a substantial increase in the number of producers of such preparations whereas the number of producers of basic colourants has remained almost unchanged.

The move to organic pigments is requiring more compounding know-how from these suppliers of colourant masterbatches and concentrates. New handling and processing technologies have to be learnt, and in some cases new equipment purchases may be necessary.

The colour compounders have to be more specific with the suppliers of their raw materials. We shall see more converters insisting on environmentally appropriate materials from the compounders in response to demands from *their* customers.

13) Flame retardants

All forecasts indicate that flame retardant consumption will continue to increase in future. This is due partly to the global acceptance of regulations on fire prevention and also to new regulations to protect people and property. In addition to environmental questions, which are gaining increasing importance in the market, the primary criteria continue to be fire safety, quality and cost efficiency of the products. The future will belong to flame retardant systems which best fulfil these criteria and sensible, practically feasible environmental requirements.

The major classes of material remain the hydrated inorganic materials plus phosphorus containing types and brominated species used in conjunction with a synergist. Antimony compounds are being strongly challenged as such a synergist by borate and stannate compounds.

In some fields, the electrical goods one in particular, there are concerns that the environmental effects of flame retardants are being given unwarranted precedence over their fire related properties for which they are selected in the first place. This could just lead to grave problems as a result of the omission of these chemicals from plastics products under certain circumstances.

14) Modifiers

Developments continue to focus on polyolefins and engineering resins - especially blends and alloys, where new modifiers are functioning as both compatibiliser and toughening agent. As a result there is less emphasis on the traditional area of PVC, although new products are reaching the market.

Many of the new products coming onto the market are designed as value-added, multi-functional products. They enhance other properties such as low-temperature performance, heat ageing and chemical resistance besides their traditional toughening role. Compared with earlier generations of modifiers, many are understood to improve flow and broaden the processing window of compounds.

2.3 Legislation

All additives are subject to some form of regulatory control through general health and safety at work legislation. Particulate and gaseous emissions are regulated this way. Other wide-ranging legislation covers the use, handling and "fitness for purpose" of all chemicals. This is especially true for sensitive uses such as food and water contact, medical or toys.

The product areas over which specific regulatory activity is relevant remain the same ones reported four years ago. These include the continuing implementation of the Montreal Protocol for ozone depleting substances and the subsequent official amendments with direct effects on physical blowing agents for plastic foams. Draft and actual EU Directives exist for volatile organic compounds; and materials in contact with foodstuffs. The landfill Directive will have implications for the disposal of plastics products, among all other waste, and reflect on the routes for subsequent recovery and recycling.

The evolution of methods of control and regulation within the States of the European Union continues from the position reported in the previous edition of this publication.

The Commission has realised that even more co-operation is needed between legislators, industry and other authorities as ever more detail is covered by regulations and other legislative instruments across all sectors of industry, commerce and society in general. This has led to a slackening of the prescriptive approach to "rules and regulations".

Life-cycle assessments or life-cycle analysis and the newer concepts of risk assessment are seen as the way forward. That is: evaluate the scenario in and through which an entity is used/performs/interacts with its environment; rather than a somewhat *in vacuo* perception of an individual chemical element, compound or species in an absolute way.

Risk assessment is then to be followed by "risk reduction" programmes within the context of a product's actual or potential application regimes. Such programmes have already been taking place for some flame retardant chemicals, solvent systems and other volatile species.

3. TECHNOLOGY

3.1 Antimicrobial Agents

Antimicrobial agents, commonly referred to as biocides all fungicides, are incorporated in plastics to provide resistance to the growth of microorganisms such as bacteria, fungi and algae. Where growth does occur it may be manifested in a variety of undesirable effects such as black pitting, pink staining and generation of odour, which are aesthetically objectionable, and loss of physical properties which results in shortened product life.

It is fortunate that most synthetic polymers are inherently resistant to microbial attack: although some, such as polysulfides, e-caprolactone polyester and polyester based polyurethane are susceptible. However, apart from the polymer consideration must also be given to the influence of compounding additives on the susceptibility to microbial attack since certain types provide the necessary nutrients to support microbial growth.

Typical of the ingredients which support growth are: plasticisers (butyrates, adipates, sebacates, laurates, epoxidised oils etc), fillers (wood flour, starch), lubricants (erucamide, oleamide, stearamide, waxes), thickening agents (starch, cellulose), oils (linseed, castor, tall etc).

Thus it will be readily appreciated that flexible PVC represents a major area of application for antimicrobial agents. The major end-use application areas where microbial attack is a problem are those involving contact with water or high humidity, such as outdoor upholstery, pool linings, boat covers, shower curtains, wire and cable coatings, sports footwear and headgear.

It is true that a large number of chemicals have been identified as having antimicrobial properties, some of which are used for other purposes in the rubber and plastics industry (such as zinc oxide, dithiocarbamates, certain antioxidants and quaternary ammonium salts), but few meet the requirements of high efficacy, low cost, compatibility with polymers and plasticizers, thermal stability during processing and long term environmental stability in service as well as being safe to handle.

It will be clear from the foregoing comments on the effects of compounding additives on susceptibility to microbial attack that the formulation of flexible vinyl compounds requires careful consideration. There appears to be general agreement that the commonly used plasticizers dioctyl phthalate, diisooctylphthalate, dibutyl phthalate, tricresyl phosphate and triphenyl phosphate are most resistant to microbial attack, whilst derivatives of azelaic, adipic, sebacic and succinic acids are most susceptible.

To perform its function effectively the antimicrobial agent must migrate to the surface and sustain a sufficient surface concentration to inhibit growth, in a manner analogous to antistatic agents. Obviously the rate of migration will be influenced by such factors as the type of plasticiser and the amount of plasticiser, the type and amount of lubricant, and the presence of other ingredients which may physically or chemically interfere with the diffusion process. Because of the active chemical nature of the antimicrobial agents the possibility of antagonism with other functional additives such as flame retardants and UV stabilizers should be considered.

The major antimicrobial agents used in PVC are now well established and include: 10,10'-oxybisphenoxarsine (OBPA), N-(trichloromethylthio) phthalimide (Folpet), and 2-N-octyl- 4-isothiazolin-3-one (OITO).