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PIGMENT DISPERSIONS

A pigment dispersion in a concentrated form is a uniform distribution of very fine color pigment particles in a suitable medium or carrier. Such a dispersion is normally used for applying color to the surface of a substrate, such as an ink film on paper or a paint film on a steel surface. It is also used for mass coloring, as in the case of plastics. Considering the high cost and specialized equipment in its preparation, a dispersion is manufactured in relatively small batches in highest concentration of pigment. The concentrate made in such a manner is usually diluted, reduced, or extended to produce the finished product.

1. Dispersion

Organic and inorganic pigment powders are finely divided crystalline solids that are essentially insoluble in application media such as ink or paint (1). The carrier used for dispersion of a pigment is usually a liquid or solid, such as a polymer, that is deformable at the processing conditions of high temperature and/or shear. The color strength of the dispersed pigment increases markedly with decrease in particle size. Optimum color strength from a given pigment in practice requires a mean particle size of the order of 0.1 μm or less, which is half the wavelength of the light involved (2). Therefore, the dispersion process involves size reduction of the pigment particle to the smallest practical size, reasonably complete wetting of its solid surfaces by the carrier, and stabilization of the resulting dispersion.

Because the intensity and color strength of pigments are largely dependent on the exposed surface, it is desirable to reduce the particles to primary particle size. This is the size of the solid pigment crystals as they are precipitated in their synthesis. In practice, the size reduction processes are limited by the nature of pigment, dispersion system, constraints of the processing equipment, the requirements imposed by the product application, and the overall economics. The maximum aggregate size permissible in a given dispersion system depends on the thickness of the film or the coating. For example, the dispersion used for architectural coatings can tolerate a much larger pigment aggregate than a similar dispersion used for automotive finishes, which requires finer particles. Any dispersion system, however, is expected to contain a very small number of these largest aggregates. Generally, it is important to reduce most aggregates to the smaller size to achieve color strength, gloss, film integrity, and durability.

In a dispersed pigment system, a primary pigment particle refers to an individual crystal and a loosely formed association of the pigment crystals from the manufacturing process. Size reduction beyond primary particle size requires excessive energy, but it also has an adverse effect on the visual properties of the pigment. Generally, the particle size of most organic pigments is much smaller initially by precipitation than optimum primary particles, but the particles tend to grow to a much larger size when their formation is complete (3–6).

Organic pigments, such as the azo red and yellow pigments, in the process of striking the color undergo definite crystal growth following their precipitation from the aqueous media (see Azo dyes). The individual crystals are joined together due to forces on the crystal surfaces to form the aggregate. These are held together as static systems by van der Waals forces. Subsequent processing to recover the pigment product results in the formation of agglomerates, which are large associations of pigment crystals and aggregates. The agglomerates are held together by forces that are much weaker than those present within the aggregates. Typically, agglomerates are joined at the edges and corners in a loose matrix form. It is possible to generate an even larger association of pigment agglomerates or flocculates during further processing. These formations are loosely held together and are usually easy to break down by application of shear. Various surface treatments are used to suppress the formation of large aggregates and, thereby, ease the dispersion process. These treatments range from the classical approach of rosination to additions of a variety of surface-active agents at the synthesis step (4, 7). However, occasionally large agglomerates, several millimeters in diameter, form during the initial stages of dispersion in a highly viscous system (8). The commercial processes used in dispersion manufacturing may not fully eliminate the aggregates. However, the design and operation of pigment dispersion equipment is aimed at application of mechanical forces to break down the agglomerates and even some less tightly held aggregates. Ideally, an excellent dispersion should consist mainly of primary pigment particles and few loosely held aggregates (9).

Wetting of the pigment surface constitutes a critical step in achieving a stable and uniform pigment dispersion. Wetting refers to displacement of adsorbed gases (usually air) on the surface of pigment particles, followed by attachment of a vehicle system to the pigment surface. Since the vehicles used for many dispersion systems are viscous, it follows that the penetration of vehicles to the pigment surface is slow and, hence, aided by external mechanical forces. Thus, the grinding (size reduction) and wetting of pigment are frequently carried out simultaneously. The adsorbed gases are displaced on application of shear, and the action also provides smearing of vehicle on the pigment surface and exposes a new surface for wetting. The system of wetted fine primary pigment particles must be stabilized to prevent reversal of the dispersion process. It is usually done by surrounding the particles with a protective colloid or buffer which blocks the reagglomeration action of particles. In some cases, the stabilization is attained by addition of ions to establish similar charges on all particles.

2. Flushing

Flushing processes are used extensively in preparing organic pigment dispersion concentrates for color printing ink applications. The process can be described as a direct transfer of pigment from an aqueous phase to an oil or nonaqueous phase without drying. When the pigment presscake is mixed with an oil-based vehicle or a carrier, water is separated from the pigment surface and replaced by the vehicle. Most organic pigments demonstrate an affinity for hydrocarbon oils and lend themselves to easy dispersion in oil by the process of flushing (see Pigments, organic). Inorganic pigments, on the other hand, have to be treated with cationic surfactants to make their surface lipophilic (10). The majority of inorganic pigments are usually dried and dispersed as dry powders in the carrier, as opposed to being flushed. Techniques used for dispersion of these pigments are different and should be treated as special cases (7, 10–13) (see Pigments, inorganic).

The process of flushing typically consists of the following sequence: phase transfer; separation of aqueous phase; vacuum dehydration of water trapped in the dispersed phase; dispersion of the pigment in the oil phase by continued application of shear; thinning the heavy mass by addition of one or more vehicles to reduce the viscosity of dispersion; and standardization of the finished dispersion to adjust the color and rheological properties to match the quality to the previously established standard.

The equipment used for the flushing process is a heavy-duty sigma blade dough mixer, generally referred to as a flusher in the organic pigment industry. The mixer is equipped with two nonoverlapping blades which can be operated at different speeds, if desired. The mixer is usually jacketed to permit heating or cooling of the mass inside. It is a heavy-duty and expensive machine, requires a high energy input, and its operation is labor intensive. Typically, the power input ranges from W/kg (0.25–0.75 horsepower units/gal) of processed mass.

Hydraulic drives, mechanical, and electronic controls are also used to achieve variation in speed of the blades for efficient processing.

When the pigment in the water phase and vehicle are mixed, the oil begins to emulsify, increasing the interfacial area. The pigment at the oil–water interphase transfers to the oil phase. As the pigment particles in the oil phase coalesce, water from the highly viscous mass begins to separate from the mixture. Ideally, the separated water is free of oil and/or pigment particles when the phase transfer is complete. The water so separated is poured by tilting the mixer hydraulically. Although 80–90% of water is removed mechanically by the process of phase transfer, a small amount of water is still present in the pigment–oil dispersion in the emulsified and trapped form. Complete removal of water from the dispersion is achieved by applying heat and/or vacuum. The process is somewhat difficult during the first step, as there is a chance that the water could emulsify with the oil phase. The clean separation of water in the first step is important to achieve the high quality of dispersion. The mechanical separation of water also removes the salts present in the pigment filter cake. Occasionally, an additional amount of salt present in the dispersion is removed after the phase-transfer step by leaching the mass with repeated additions of water. The mechanism of flushing is well established in the industry and has been described in various publications (15, 16).

Flushing is frequently used for the manufacture of large quantities of a dispersion having a specific pigment in a compatible vehicle system. The flushed products, typically containing 28–40% pigment, offer sufficient flexibility to the formulator to produce the finished offset ink. The flushed products exhibit superior gloss, transparency, and strengths, compared to those produced by dispersing the dried pigment. Flushing is particularly important to dispersions of organic pigments, such as Diarylide Yellow (CI Pigment Yellow 12, CI 21090) and Alkali Blue (Pigment Blue 61, CI 42765) because the drying process is detrimental to the product quality of these pigments.

3. Equipment

Various types of equipment are used commercially to manufacture dispersed pigment concentrates or finished dispersion products used by printing ink, and the coatings and plastics industry.

3.1. Kneaders or Internal Mixers

Kneaders are designed to process materials and mixtures with high plastic viscosity, ie, up to $10\ \mathrm{Pa{\cdot}s}$ (100 P). Dispersion of pigment is accomplished by kneading the process mass containing pigment, water, and vehicle. The mechanical energy is transferred throughout the high viscosity mass by internally developed shear. Typically, the mixer is equipped with two parallel helical blades rotating in the opposite direction at different speeds in a contoured vessel. The blades and the mixer are machined to a high degree of precision to keep the clearance between the blades and between the blade and the vessel wall as low as possible. The wiping action of the blades produces a high degree of shear. The mass continuously undergoes the action of folding and unfolding by the opposing pitch of the mixing blades. The system formulation is controlled to develop a high plastic viscosity, which allows transfer of mechanical energy between the moving blade and the vessel wall. The bulk of the water separates from the mass as a clean aqueous phase and is poured off by tilting the mixer hydraulically. Small amounts of remaining water are removed under vacuum, leaving behind a highly viscous mass of pigment in the vehicle. Considerable heat is generated during the process, and it is removed partially by circulating water in the jacket and adjusting the viscosity of the mass, by addition of thinners and oils, to regulate the energy input.

The heavy-duty sigma blade batch mixer is used widely for the process of flushing in the preparation of pigment dispersions, primarily for offset inks. For some products, it is also used to disperse dry pigments in liquid vehicles of a wide range of viscosity and in thermoplastic resins with relatively low melting points. The finished dispersion from the flusher can be discharged as a solid or liquid with a wide range of viscosities. The mixer offers a wide operating range of pressures, temperatures, and speeds of blades. This processing flexibility makes it an extremely versatile machine for processing a wide range of dispersions and explains its popularity for producing pigment dispersions for offset inks, despite its high installation and operating costs. The mixers are routinely available to 3774-L (1000-gal) capacity and can process up to 3200 kg of finished dispersion. The choice of construction material ranges from carbon steel and chrome-plated carbon steel to various stainless steel alloys. Often the mixers are hydraulically driven to operate under constant torque and permit operation with variable speeds at different stages. Due to very specialized construction, close tolerances, and large drive motors, the installations require high capital investments. The process is batch-type and can take several hours to complete. Considering the high capital and operating costs, alternative continuous processing systems have been explored to produce similar dispersions. There are, however, few successful commercial installations.

A two-roll mill can be considered as an internal mixer due to a large clearance (up to 15 mm) between its rolls. The process mass is subjected to kneading just before it enters the nip between the rolls. Two-roll mills are used to prepare pigment dispersion in elastomers and thermoplastic resins. In some cases, the pigment and the medium is premixed; in others, the resin is banded on one roll and the pigment is added. This type of equipment provides good control of the plastic viscosity, resulting in high quality dispersions. The rolls are parallel and rotate in opposite directions. The degree of shear can be varied by varying the roll speeds, the distance between rolls, and the temperature. The operating temperature is controlled by circulating water or steam through a core of rolls. Electric resistance heaters or hot oil circulation is used if very high temperatures are required. Two-roll mills are heavily powered to subject a small mass to high energy input to achieve the desired dispersion in a short cycle time, typically a few minutes. The equipment is used to produce small quantities of concentrates and, as such, has limited commercial applications (17).

3.2. Close Tolerance Mills

This class of dispersion equipment can be classified into low speed cylindrical roll mills and high speed disk or cone mills. Cylindrical roll mills are used for processing pigment dispersions in the paste form for ink and paint applications. Processing viscosities are relatively moderate, compared to the mass processed in flusher, and range from $20 - 1000$ Pa·s (200–10,000 P). The cylindrical roll mills comprise multiple, parallel rotating rolls powered by a single drive motor. As many as five adjacent rolls rotating in opposite direction to each other have been used, although three rolls are most common. A good premix of pigment and vehicle is fed to the nip of the slowest moving rolls and removed by a doctor blade from the fastest moving rolls. The clearance between the rolls is typically 10–15 μm, requiring high precision in the manufacture of the rolls. The clearance between the rolls decreases successively from the feed end to the product end. This decreasing nip clearance and the increasing rotational speeds of the subsequent rolls exert very high shear on the material passing through the nip. The inward rotation of the rolls forces the process mass toward the nip, and the bulk of it is forced back up and continually dragged back toward the nip. This flow pattern creates a high degree of mixing and shearing. Mathematical expressions have been developed for horsepower requirements, throughput, and applied work, and have practical applications in operation of the mills. The rolls are cored for circulation of cooling water or steam. The construction of the rolls is robust, with the roll surface machined to a high degree of precision so that it runs parallel with unchanging gap over the entire length of the roll. The rolls are machined to have a slight degree of convexity (crown) to account for operation at temperatures of 60°C and higher and under high pressure.

High speed stone and colloid mills achieve dispersion by smearing action. The equipment consists of two accurately shaped carborundum stones, one stationary and the other rotating at high speed (3600–5400 rpm) with a small gap separating the stones. The shear applied to the mass flowing between the stones under laminar conditions provides the dispersing action. Although the colloid mill is designed primarily to produce emulsion-type colloidal dispersion, it is also used for preparation of pigment dispersions. The rotors are in the form of disks, or truncated cones, rotating at 3000–5000 rpm. The dispersion is fed by gravity, and often the flow in the machine resulting from centrifugal force is aided by the feed pump. The viscosities are typically moderate at $10\ \mathrm{Pa{\cdot}s}$ (100 P) or less. The energy input depends on the gap (clearance between stator and rotor), surface roughness, and rheological properties of the process material (17).

3.3. High Speed Fluid Energy Mills

This type of equipment is used primarily for preparation of relatively low viscosity mill bases for inks and paints. The first is an impeller type which achieves dispersion by the application of shear. The second type is in the form of a rotor–stator, and the dispersion is achieved by impingement or impact.

The high speed disk disperser consists essentially of a circular saw blade-type impeller mounted vertically in a cylindrical tank. The rotational speed of the impeller is very high with a common peripheral (tip) speed of 5000 ft/min (18). Various impeller designs are available, depending on the type, size, and direction of angle of the serration along the rim. Frequently, a dual shaft agitator system, consisting of a low speed anchor agitator mounted centrally in the tank and the high speed disperser mounted off-center, is used to provide good mixing and dispersion. Since the dispersion is achieved by shearing action, the mixer becomes effective at high viscosities, such that a sufficient flow is maintained in the tank with a flow pattern resembling a rolling doughnut within the tank. The high viscosity is usually obtained by increasing the pigment solids in the dispersion, rather than increasing the vehicle viscosity. Also, the typical application involves mixing the dry pigment in the vehicle, and wetting the pigment surface by penetration, leading to choice of vehicles with relatively low viscosity. Considering the mild dispersing action of this impeller, compared to the other equipment described previously, such as flushers, the use is limited to easily dispersed pigments. A lot of empirical work has been done to provide the guidelines for formulating dispersions, specifically for high speed disk disperser blades. The disk disperser is also used to prepare a premix or a mill base, which is processed further to obtain a finished product.

The high speed dispersion mill is based on impingement action. A kinetic dispersion mill, eg, the Kady mill manufactured by Kinetic Dispersion Corp., is a typical example of this type of equipment. The mixer is a rotor–stator combination mounted vertically in a cylindrical tank. The slotted stator fits like a collar around the slotted rotor with clearance between the stator and rotor of less than 2 mm. The peripheral velocity (tip speed) of the rotor is very high, typically ranging from 40–50 m/s. The pigment–vehicle mixture is drawn in from the top and bottom of the mill head and forced through the slots in the rotor–stator by centrifugal force. The break-up and attrition of the pigment aggregates occur as a result of forceful impact. The suspended solids emerging from the rotor slots at high velocity are subjected to additional impact against the stator wall and against each other. Because the disintegration of large particles occurs by impingement rather than by shear, the formulations using low viscosity vehicles can be used, exploiting more effective penetration and melting properties of such vehicles. The vehicle solids can be added after the dispersion is complete to achieve its stabilization.

3.4. Ball and Pebble Mills

A ball or pebble mill is essentially a cylindrical container partially filled with metallic or ceramic grinding media in the form of balls or pebbles. The mill base, consisting of pigment and vehicle, is charged to the mill. Grinding and dispersion takes place because of impact and shear resulting from the cascading action of the balls when the cylinder is rotated around its horizontal axis. The ball mills and the pebble mills are differentiated on the basis of the nature of grinding media and the liner. Ball mills typically use metallic media (cast iron or alloy steel), and the liner is constructed out of alloy steel or some other special material. On the other hand, pebble mills utilize ceramic media and are lined with a nonmetallic liner, such as ceramic or rubber. The efficiency of the ball mill depends on a number of physical factors, such as size and speed of the mill; size, density, and loading of the media; and load, viscosity, and composition of the mill base. The mill is typically operated at a speed which induces a cascading action of the balls. The optimum angular velocity is a function of the critical speed, the speed at which a complete centrifugation occurs. The optimum speed is $20.35/\sqrt{r} - 1.75\sqrt{r}$ where r is radius in meters.

The loading of grinding media is typically 40–50% of the mill volume, whereas the mill base is about 20%. The dispersion technology in the ball mill is fairly well understood, and high quality products are routinely manufactured using the ball or pebble mills in the paint and ink industry (19). It is a versatile piece of equipment suitable to carry out premixing and dispersion steps in a single machine. The maintenance costs are usually low, and although it is batch processing equipment, it requires virtually no supervision to operate. It also offers wide latitude in formulations, from the standpoint of viscosity and pigment loading, and can handle pigments that are hard to disperse. The main disadvantage of this type of equipment is that it is rather bulky, and considering its long batch cycle time, has limited throughput. Ball and pebble mills have dominated in the dispersion of paints and inks over the past 50 years. The trend has been to change the manufacturing processes from the ball mills to the continuous processing systems, based on media mill, because of their higher throughput and ability to process high viscosity bases.

Some modifications in the basic concept of the ball mill has led to the development of attritors and vibration mills (20, 21). The attritor consists of a vertical grinding chamber equipped with an agitator. The agitator basically includes a set of horizontal fingers attached to the central shaft and provides the necessary action for dispersion by vigorously agitating the grinding media. The equipment can be operated as a batch or continuous processing system. The continuous processing system is equipped with a recirculating pump for the mill base. It is claimed that an attritor can reduce the cycle time significantly, compared to the ball mills. The higher efficiency can be attributed to the fact that all of the grinding media is in constant motion, unlike the media in the ball mill. Typically, the media used in the attritors is 0.3175–0.476 cm, which is smaller than that used in the ball mill.

3.5. Sand, Bead, and Shot Mills

Sand, bead, and shot mills have replaced the ball and pebble mills in many applications. This class of equipment can be broadly termed as media mills. They have gained in popularity largely because they require less space, are capable of operating continuously, have higher specific energy input, and consequently have much higher throughput when compared to a ball mill with comparable capital investment. They can be regarded as a logical extension of ball (pebble) mills and then the attritors. Generally, the media mill consists of a cylindrical, jacketed chamber fitted with a high speed agitator. With the exception of the sand mill, the media mill can be positioned vertically or horizontally. The chambers are filled anywhere from 65 to 90% of the gross volume with grinding media. The earliest version of this type of equipment was a sand mill, which utilized fine 840–590 μm (20–30 mesh) Ottawa sand. The dispersion or mill base is introduced at the bottom with a product overflow from the top. The separation of the media from the product is aided by a screen in the outlet. The intense agitation of the fine media provides multiple contacts for the pigment agglomerates, and size reduction and dispersion of the solid takes place by a combination of smear and impact. The processing temperatures can be controlled by use of a heating or cooling medium. The operation of sand mills is limited to atmospheric pressure; hence mill bases with volatile solvents, or those at high viscosity, cannot be handled.

The bead and shot mills have overcome some of the limitations inherent with the design of sand mills. The bead and shot mills are similar in construction and differ only in the fact that bead mills use ceramic or glass media, varying in size from 0.3 to 3 mm, whereas shot mills use similarly sized carbon steel and alloy steel shots in addition to ceramic media. Depending on the application, a horizontal or vertical type of mill is used. The vertical mills are simpler and robust in design, exhibit higher throughput, and are better suited for a wide range of viscosity bases. The media mills in horizontal and vertical configuration have been extensively used in the paint and ink industry for dispersion of pigments. The horizontal mill offers the benefits of uniform distribution of media, ease of starting with large chamber volume, and ease of serviceability. The chamber volume ranges from 0.25 L for a laboratory size mill to as large as 500 L for large-scale industrial installations. The agitator is configured in the form of a series of flat disks with holes or a series of pins. The tip speed varies between 12–20 m/s. The separation of media from the dispersion is accomplished by cylindrical sieve cartridges or rotating gap separators. Application of the gap separator is usually limited to a media size of 1.00 mm or greater. The slot width (gap) has to be less than half of the average bead diameter. The trend has been toward bead sizes of $\leq$0.5 mm to achieve the dispersion quality needed. The quality of dispersion and the specific energy input is influenced by the size, hardness, and density of the media, tip speed, media loading, and viscosity of the mill base (22). Advances in media mill technology include use of a milling chamber in the form of a narrow annular space allowing extremely high specific energy input (23, 24) and novel designs of media separators (22). The quality and production costs of the dispersed products manufactured using the media mills have improved significantly in the 1990s, but capital costs of the sophisticated installation has also risen steadily. A significant amount of work has been done to develop a mathematical model of the process in the media mill as applicable to the dispersion of pigments (25).

4. Uses

The formulation of dispersed pigment concentrates is influenced by the manufacturing process, as well as the performance parameters desired in the final application. The finished product in many cases is significantly different in formulation than the concentrate to achieve desired properties. One of the principal factors to be considered is the concentration of pigment in the dispersion concentrate. Compatibility of the carrier (solvent additives, etc) used in the preparation of concentrated dispersion and that used in the finished color product also plays an important role. In some cases this can be difficult because the carriers having the best performance, from the standpoint of processing, could be poor in the application systems. However, in the majority of the applications, particularly in coatings and colored plastics, the concentration of the pigment in the finished product is quite low, and the incompatibility problem is easily overcome.

Generally, the pigment dispersion concentrates are formulated for specific end use. They can be supplied as flushed pigments, dispersions or pastes for offset inks, chip dispersions for solvent and aqueous inks, and color concentrates for coloring large quantities of plastics. Although it is feasible for the end user to prepare the pigment dispersion concentrates, it is usually more cost effective and technologically advantageous to manufacture these dispersions by the pigment manufacturers of specialty dispersion houses. Three significant areas of application for concentrated dispersions, ie, printing inks, coatings, and plastics, are considered in the following.

4.1. Printing Inks

The consumption of dispersed pigment concentrates in the form of flushed color pastes is substantial in the manufacture of offset printing inks inks (qv). The film thickness of the ink film on the substrate (usually paper) ranges from 0.002 to 0.01 mm. The concentration of pigment in a typical ink formulation is relatively high at 8–20%, depending on the type of pigment and end use. Therefore, dispersed pigment concentrates are formulated at very high pigment level to permit the flexibility in formulation of the printing ink products. For example, the flushed color concentrates used in offset printing inks are formulated with pigment concentration ranging from 20 to 50%. These are extremely heavy viscous pastes with viscosities ranging from 100 to 10,000 Pa·s (1000–100,000 P). In some applications, the dispersed pigment concentrate is in the solid (chip) form, containing 40–70% pigment in a carrier resin, such as nitrocellulose. These are converted to finished inks by dissolving the solid concentrate in the solvent, rather than by thinning or dilution.

Table 1. Estimated 1991 Consumption of Printing Ink Colorants by Form and Type of Ink, 10^6 kg

Type of ink	Dry[a]	Flushed[b]	Resin bonded[c]	Solvent dispersion (dry basis)	Chip	Presscake[d]	Total
letterpress	0.14	0.91	0.0	0.0	0.0	0.0	1.1
lithographic	0.86	16.5	0.0	0.0	0.0	0.0	17.4
gravure	5.09	0.18	0.27	1.05	2.27	0.86	9.7
flexographic	2.0	0.0	0.45	0.64	0.27	7.0	10.4
other	1.54	0.23	0.59	0.0	0.36	0.0	2.7
Total	*9.63*	*17.8*	*1.31*	*1.7*	*2.91*	*7.9*	*41.3*

[a]Includes easily dispersed pigments.
[b]Including fluorescent pigments for lithographic inks.
[c]Includes fluorescent pigments for gravure, flexo, and screen inks.
[d]Includes aqueous dispersions.

The high pigment level in the concentrates permits use of high shear to obtain quality dispersions. Moreover, it allows greater economy for distribution of the concentrated products to the ink manufacturers. Most manufacturers of pigment concentrates or flushes in the United States offer a wide variety of products in liquid, paste, or solid forms, containing the specific pigment in the carrier or solvent compatible with most common types of inks, ie, letterpress, lithographic or offset, solvent gravure, and flexographic (packaging) inks. The estimated market for printing ink colorants, other than carbon black, extenders, and titanium dioxide, was 41.3×10^6 kg, valued at \$501.1 million. The estimated 1991 consumption of colorants in these four types of inks by form and type of ink is given in Table 1 (26).

In the United States, the bulk of color oil inks, ie, letterpress and lithographic, are manufactured from dispersed organic pigment concentrates, usually in the flushed paste form. The flushed colors are usually manufactured by the pigment manufacturers and supplied to the printing ink producers for conversion to the finished form. These flushes are formulated specifically for a particular application. For newspaper inks, where the ink film setting occurs mainly by penetration of oil in the papers, the pigment flushes use predominantly mineral oil and a small amount of resin for wetting the pigment. The pigment flushes for lithographic ink application (heatset and quickset) are formulated with a specific resin system and carrier solvent to permit printing with the least amount of emulsification. Lithographic inks, based on setting of film by application of heat, are prepared from the flushes that typically contain synthetic or modified natural resins dissolved in hydrocarbon oil ($\text{bp} = 220 - 280^\circ$) and other specific additives. The ink film is cured by a combination of setting the resin system and evaporation of hydrocarbon oil. Flushes used in the manufacture of quickset inks are formulated with pigments in the carrier system containing synthetic resin, drying oils, and low viscosity nondrying oils. The film is initially set by penetration of low viscosity oil in the substrate, followed by oxidative polymerization of the resin and drying oils (qv) (27, 28).

Gravure inks, typically used for long press runs, are very fluid (low in viscosity) and dry by evaporation of solvent, leaving behind an ink film ca 10-μm thick. Gravure inks are manufactured by milling dry pigment in the carrier system, consisting of volatile aromatic solvent, such as toluene, binders, and synthetic resins. Inks made by this procedure typically follow the sequence of shot milling the concentrate at a high pigment level ranging from 25–35%, followed by thinning the concentrate with the addition of solvent, resin solution, and other additives. Gravure inks are also manufactured from dispersed pigment concentrates in the form of resin chips by dissolving them in the carrier solvent system. The bulk of gravure inks, however, are manufactured with dry pigment as a starting material (27, 28).

Flexographic inks are similar to gravure inks in that they are formulated as resin–solvent–pigment systems of low viscosity, and they dry by evaporation of solvent. The flexographic printing process differs from gravure printing in that it is based on the use of rubber rollers and plates and restricts the choice of solvents to low boiling alcohols and water in combination with oxygenated solvents. Dispersed pigment concentrates are used, similarly to gravure systems, except for differences in solvents and resins, which are principally acrylic polyamide, alcohol soluble nitrocellulose, and shellac (28, 29). Concentrates in the form of solid chips are available in the market for aqueous inks suitable for textile printing. The chip typically contains 60% organic pigment and 40% of water-soluble acrylic resin. The chip is solubilized in an aqueous color base that can be combined with various compatible textile print clears to produce a finished textile ink (30).

4.1.1. Outlook

Total 1991 U.S. ink consumption was estimated at about 86×10^7 kg valued at over $3.0 billion. The demand is estimated to grow at an average of about 3–4% per year in volume (26). The principal changes expected in the 1990s will continue to be in response to environmental and safety concerns and government regulations. The bulk of printing inks use raw materials based on fossil fuels, such as coal (qv) and petroleum (qv). Consequently, their cost and availability are an important factor influencing the direction in which the industry heads. Manufacturers of dispersed pigments must make appropriate changes in their product formulations to meet the demands of lithographic and letterpress ink businesses. The emission of volatile organic chemicals (VOCs) in the press room has increasingly led formulators of lithographic inks to innovative formulations. Also, the quicksetting ink applications use of irradiation is increasing to accelerate the oxidative polymerization process of film setting (29).

The flush colors for heatset inks are formulated with decreasing quantities of deodorized solvent or mineral ink oils, in response to the trend toward higher solids concentration in the ink, and consequently lower volatile compounds. There is a growing market for flushed colors containing soybean oil replacing a portion of mineral oil in the formulation (29, 31). The benefits (eg, low emissions) of soya-based inks, use of renewable resources, and some enhancement in color properties have long been available in products with other vegetable oils, such as linseed or tung oils, both of which have been available for decades.

Although safety and environmental concerns have encouraged manufacturers to develop formulations based on aqueous pigment concentrates, such inks have not been widely accepted in high quality solvent gravure printing processes. The use of aqueous inks is largely limited to flexographic printing processes.

4.2. Coatings

Coatings (qv) generally exhibit heavier films, a fraction to a few millimeters thick, and are significantly lower in concentration of pigment. Dispersed pigment concentrates are therefore lower in pigment concentration and easier to reduce to the final product, when compared to similar dispersions prepared for offset inks. The concentrates are formulated to meet rather demanding performance specifications of the coated systems. The superior performance required for cooling systems is due to expected durability in (frequently) severe environments.

The use of water-based coating systems has grown steadily during the 1980s due to growing environmental concerns, but also because of continued improvement in the performance of such systems. Several additives are required in aqueous dispersions for coatings, including the dispersants tailored for the type of pigment used. Emulsifiers and thickeners to prevent settling of solids and preservatives to prevent bacterial growth during storage are also needed. The concentrates range from 20–40% pigment. Frequently, concentrates and the finished products are manufactured by the same dispersion house and many times at the same location.

4.3. Plastics

An estimated 12–16% of total U.S. organic pigment goes into these markets. Organic pigments, because of their generally poor heat stability, find somewhat limited use, but a few organic colorants can withstand high processing temperatures and have adequate lightfastness and bleed resistance for application in plastics (see

Colorants for plastics). Among them are diarylide yellows, phthalocyanine blue and green, permanent red 2B, quinacridone, and perylene (32). Pigment dispersions, commonly known as color concentrates, are used in the plastic industry and show a wide variation in the pigment concentration and physical form. Color concentrates in various forms, ranging from liquids to solid granules, are metered directly in the processing equipment, usually by an extruder to incorporate color into the plastic process mass. The solid concentrates, however, are premixed with clear plastic prior to feeding the processing equipment, where both are melted and intensely mixed. Although the pigment concentration in the final product varies, depending on the nature of the application, it is usually quite low ($<1\%$ by weight), except in the case of very thin opaque plastic films. Extruders are typically used for reduction of color concentrates.

The color concentrates are manufactured, either by incorporating dry pigment in a compatible resin system in a high intensity mixer, or by the classical flushing process, wherein the pigment presscake is flushed with a low melting resin, followed by cryogenic grinding of the solid mass in the kneader (33). The latter process is claimed to be superior for pigments that are harder to disperse by conventional processes. Typically, the pigment content of the concentrate is between 10–50%. The resin used as a carrier needs to fulfill two principal requirements. It should have good wetting characteristics for the pigment for which it is used. Secondly, the carrier, which is usually a low melting thermoplastic, should be compatible for the thermoplastic polymer for which the concentrate is intended. A number of other dispersants and additives are used for the treatment of pigments to develop superior dispersion properties (34, 35). Color concentrates in the pellet form are used most widely for coloring thermoplastics, particularly low density polyethylene (LDPE). The addition of pigment in high concentration changes properties of the carrier resin significantly. Specifically, concentrates become more difficult to melt because of the reinforcing effect of the pigment. Ideally, the melting point of concentrates should be similar to that of the unpigmented polymer. Hence, resin with a somewhat lower melting point than the target resin is chosen as a carrier resin for color concentrate.

The choice of a pigment for a specific plastic application also depends on its resistance to solvent and its insolubility in the polymer used. The phenomenon of migration, which includes the effects of bleeding and blooming, results from the partial dissolution of pigment in the polymer system at the processing temperature. Organic pigments generally satisfy the lightfastness requirement, but it is possible that a certain pigment may fade badly on exposure to light, although it is perfectly stable in the other dispersion systems.

Organic pigments are selected for applications, such as films and fibers, in which transparency and high tinctorial strength are desirable. Inorganic pigments, on the other hand, are preferred for those applications in which hiding power or opacity and high light- and weather-fastness are critical factors. Frequently, the two types are combined to take advantage of each economically. The following discusses the primary types of plastics with regard to preparation of pigment concentrates.

4.3.1. Thermoplastics

The highest consumption of color concentrates is in thermoplastic resins, such as low and high density polyethylene, polypropylene, PVC, and polystyrene. Processing techniques for thermoplastics are usually based on dry color dispersion in a compatible resin (36).

A wide variety of color concentrates are available for coloring rigid and flexible (plasticized) poly(vinyl) chlorides (PVC). Color concentrates for rigid PVC are made by dispersing a pigment in the resin. The flexible vinyls, on the other hand, use either concentrates made in plasticized resins or in a plasticizer, such as dioctyl phthalate (DOP) which is a liquid. The dispersions in the plasticizer are produced as a paste on a three-roll mill. The pigment concentration in the paste is typically 20–35%. The solid color concentrates for PVC are produced from free-flowing granules to a very fine powder (see Vinyl polymers, vinyl chloride and PVC).

Polyolefins are manufactured and used in much greater quantity than any other class of plastics. The principal polyolefins are polyethylenes of various densities (LDPE, LLDPE, HDPE) and polypropylene (PP) (see Olefin polymers).

The processing temperatures range from 160–260°C for LDPE to 220–300°C for PP. As a result of high processing temperatures, and consequently a high degree of softening, the shear force available during processing for the dispersion of pigment powder in polymer melt is limited. Therefore, pigment concentrates prepared in compatible polyolefins are frequently used. Color concentrates in the granulated form not only exhibit superior tinctorial strength, but also improve the safety of the operation. A number of mixing and processing techniques are used to manufacture the concentrates. They are manufactured in high and low density resins in internal mixers, two-roll mills, or sometimes in extruders. Dispersions in low molecular weight (polyethylene) grades are made by flushing techniques. Concentrates for film need the highest degree of dispersion, whereas those for injection molded articles may sacrifice dispersion quality for economy. The selection of pigment is done on the basis of its heat stability and tendency (or lack thereof) to migrate. Polypropylene color concentrates are more difficult to produce, due to its higher processing temperature and sharper melting points resulting from its crystalline structure.

Polystyrene (PS) is a highly rigid, glass clear, and almost colorless thermoplastic resin which softens between 80–100°C, and has a typical processing temperature range of 170–280°C. It is relatively easy to color; a significant volume is colored directly from pigment rather than dispersion concentrates. An adhesion or wetting agent is frequently used in conjunction with organic pigments for coloring polystyrene. Impact-resistant polystyrene containing typically 5–20% natural rubber is used widely for house appliances and products requiring good impact resistance. These are usually colored using the color concentrates. The concentrate manufacturing techniques are similar to those used for polyolefin. Copolymers of polystyrene with acrylonitrile and butadiene (ABS) are highly opaque, whereas polystyrene and styrene–acrylonitrile (SAN) are highly transparent. The choice of pigment used for coloring also depends on the opacity of polymer to be colored. Color concentrates for a polystyrene type in the paste form afford the ease of metering and blending various colors to obtain the required shade. Their applicability is somewhat compromised by the fact that their liquid component affects the mechanical properties of the finished colored plastic.

Dispersed pigment concentrates are available in a wide variety of other thermoplastic resins. Thermoplastic polyurethane (TPU) is used by the same organic pigments used for plasticized PVC. Dispersed pigment concentrates in carrier resins such as vinyl chloride–vinyl acetate copolymers, low molecular weight polyethylene, and PU itself are also used. Concentrates in the paste form, with pigment content ranging from 20–40%, are prepared by dispersing dry pigment powder in the PU solution in a ball or media mill. Other commercially available thermoplastics include polycarbonate, polyamides, poly(ethylene terphthalate) (PET), and cellulose derivatives. Pigmentation of these thermoplastics largely follows the same procedures as described above.

4.3.2. Thermosetting Plastics

Thermosets are processed only once, using heat and pressure to form semifinished or finished articles. The coloration of these plastics is generally accomplished using paste color dispersions. The colorants are worked into liquid resins before curing. Ball mills are commonly used to color prewetted molding powders prior to hardening. Dispersions for coloring epoxies are required to be free of water because the presence of water affects the curing role and hardeners of the resin. The dark color of phenolic resins restricts the coloration of these resins. Pigment dispersions used for thermosetting plastics are typically inorganic browns, reds, and greens. Coloration of unsaturated polyester and multiacrylic resin is performed with pigment–plasticizer (DOP) pastes. Occasionally, the pigments are directly dispersed into a small amount of monomer.

4.4. Coloration of Synthetic Fibers

Techniques of mass coloration or spin drying of synthetic fibers, particularly polyolefins, lie between the textile and plastic area. It is distinct from textile dying methods in that the material is colored before it is extruded. Pigment dispersion concentrates are widely used, considering their superior quality of dispersion when compared to incorporation of dry pigment powders, even if their average particle size is 2–3 μm. Large particles cause filament breakage and clogging of the spinnerette dies. As in the case of thermoplastic resins, the heat stability of the pigments used is critical. Spinning temperatures as high as 300°C used in melt spinning limit the use of only certain pigments. Pigment concentrates are made in the compatible polymer by the techniques described earlier. Polyolefin fibers, particularly polypropylene, represent the largest market for dispersed pigment concentrates (see Fibers, olefin fibers).

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