See The Difference We Make

Increasing Pigment Black Jetness with Color Pigment Blending

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Abstract

Carbon black is one of the oldest manufactured materials. It is a soft, fine, black powder, dating back to our prehistoric ancestors, who utilized black pigment from soot. Carbon black is still used for various aspects of modern life. It can be found in inkjet printer ink, natural and synthetic rubber, used as a filtration material and in coatings, plastic, and ink applications. From a coloristic perspective it is hard to quantify black using conventional L*a*b* parameters and so three specific metrics have been developed to quantify the color quality of black. This includes Blackness [My], Jetness [Mc] and Undertone[dM]. It is often assumed that black is only one shade, but in fact there are many shades of black and good coloristic control of them is key in the manufacturing industry. Manipulation of the shade and depth of black is important to achieve the “blacker than black” shades often desirable in paint and plastic items. This paper will focus on the manipulation of jetness and shade of carbon black using different color pigments. Jetness is the color dependent black value, developed by K. Lippok-Lohmer, which is a complex function of surface area, primary particle size and degree of dispersion. Where smaller particle size correlates to a higher degree of jetness.

The purpose of this study is to determine if the addition of secondary color pigments will increase the maximum jetness of a black pigment. The paper will begin by investigating the optimum loading of carbon black to achieve the maximum jetness. This will be conducted by dispersing pigment samples in LDPE at increasing intervals of 0.1% and analyzing the resulting color data. Once the optimum loading of each carbon black sample is determined, the incremental addition of secondary color pigments i.e. Pigment Blue 60, Pigment Blue 15:3, Pigment Green 7, Pigment Red 179 and Pigment Violet 29 will be investigated, in order to determine the effect they have on the initial jetness, blackness and undertone. The difference between the hue of the color pigments used will also be investigated to understand whether a blue shade black appears “blacker” than a red shade black.

Introduction

Carbon Black is the blackest industrial colorant produced from raw material chemically consisting of more than 95% pure carbon along with small quantities of oxygen, nitrogen and hydrogen[1]. In early civilizations, the by product, soot (also considered carbon black) was used in cave paintings in ancient China and Egypt for writing ink. Now carbon black is made in specifically designed reactors producing different grades varying in particle/aggregate size, surface area and structure for many applications[1]. This pigment can be found in many modern industries such as in the automotive industry where carbon black makes up approximately one fourth of the weight of the average automobile tire[3]. It is also used in cosmetics for eyeliner, lip stick and nail enamel. Also, in printing ink, paint, and paper along with in protective coatings, plastics, and resistors for electrical circuits[3]. It is a widely used pigment. Carbon black is produced in the following several processes:

Oil furnace or furnace black process: In this process, aromatic oils are combusted in a controlled atmosphere at high temperatures in a closed reactor thus producing carbon black and tail gas. These temperatures can range from 800ºC to 1200ºC[4]. During this process, fuel is atomized and then sent to the reaction chamber to start carbonization. Oxygen levels are maintained to prevent the formation of soot[4]. Primary particles are then formed when the tail gas is removed allowing the carbon atoms to begin to bond to their neighbors within the droplet during the solidification process[1]. As the droplets leave the reaction chamber and through the furnace, they may encounter other droplets forming a carbon black aggregate[1]. The carbon black produced goes through the flight of the reactor, are cooled by water sprays, and then collected in bag filters. This is the most widely used process in the world compromising of over 80% of all carbon black production[4].

Thermal Black process: In this process methane is injected into the furnace where it decomposes into carbon black and hydrogen[1]. The carbon black produced has the largest particle size and the lowest degrees of particle aggregation or structure[1]. This process also produces one of the purest forms of carbon since it is made of a natural gas[1].

Lamp Black: This is the oldest process in producing carbon black which was formally from oil lamps[1]. Oil is burned on a cast-iron pan in a furnace as heat radiates from the hood resulting in the vaporization and partial combustion of the oil which is then mostly converted into carbon black[1].

Acetylene Black: In this process high purity carbon black is produced in closed reactors from the decomposition of acetylene[1]. This carbon black is in powder form and is impossible to pelletize[1]. It is also used as a conductive black in electric cells, antistatic rubber, plastic applications, and cable manufacturing due to its very high thermal and electrical conductivity quality[1].

Carbon black is a very fine powdered pigment, and there are three main properties of carbon black that play a significant role in the characteristics of the final product and guide selection of a carbon black for an application.

1) Primary particle Size: Particles are usually spherically shaped and can be as small as 5nm[4]. The particle size determines the blackness and dispersibility of carbon black when mixed in resins and vehicles[1]. Smaller particle size gives higher blackness although dispersibility becomes more difficult due to the increase in coagulation force[1]. Larger particle size gives lower blackness, but dispersibility is improved, the surface will wet more easily, and electrical conductivity is increased[4].

2) Structure of the carbon black: Carbon black is composed of fused primary particles that form complex clusters called aggregates approximately 50nm in size which further clump together into chains of agglomerates[4]. The size of these structures plays a significant role in the wettability and dispersion when used in mediums such as coatings, paints and inks[4]. The structure of the carbon black provides competitive grade differentiation among carbon black manufacturers, who control the properties[4]. Larger structure gives better dispersibility, lower blackness and better conductivity, so it can be used to engineer carbon black grades[4].

3) Surface area: It has a strong influence on the blackness and is related to particle size[1]. Smaller surface area and bigger particles have lower tinting ability as a pigment with a brown undertone[1]. Higher surface area and smaller particles gives higher tinting strength and has a bluer/blacker undertone[1].

Carbon black is known to be difficult to disperse. Dispersibility is dependent on the structure, shape, and porosity of the carbon, it can be difficult to obtain a successful dispersion. This is due to carbon's strong tendency to re-agglomerate during the dispersion process due to Van der Waal forces. It is critical to break up the agglomerates into aggregates to achieve an adequate dispersion and often, additives are used to stabilize the dispersion.

Research Objective

The purpose of this study is to investigate jetness, blackness and undertone of carbon black and then research the effect the addition of different secondary colors have on each metric along with the quality of black that is obtained. This allows us to investigate and quantify the different shades of black. Answering possible questions such as what is the difference between a blue shade, green shade, or red shade black and how exactly is this difference measured? We aim to understand if a formulator is working with carbon black, would the addition of colored pigments make the end-product more appealing to the consumer? An example of this application of this would be allowing different parts of an item to match or be manipulated like the parts of a Canon Camera or office chair.

Ultimately the color produced by carbon black is determined by primary particle size, structure, and surface area. Usually color is quantified using a colorimeter or spectrophotometer which provides L*a*b* values. Due to the dark qualities of carbon black this method is difficult to use as the CIE L*a*b color space is very compressed for dark colors and not accurate. So, three specific metrics have been determined to provide information of how black is black. The three metrics used to quantify the color quality of black are Blackness, Jetness and Undertone[2]. These metrics are determined using a spectrophotometer which provides Tristimulus values (X, Y, Z) that are used to further calculate for each metric. Blackness [My] is a measure of the degree of blackness and is directly related to the reflectance[2]. Jetness [Mc] is the color dependent black value[2]. It is a complex function of primary particle size, surface area and degree of dispersion[2]. So, carbon blacks with smaller primary particle sizes usually have a higher degree of jetness than those with larger particle sizes. Undertone[dM] quantifies how neutral the black pigment and binder are by providing a value that indicates either a brown-reddish or blue undertone[2]. The formulas for each are as follows:

Blackness [My]= 100*log (Yn/Y)

Jetness [Mc]= 100*[log (Xn/X)-log (Zn/Z) +log (Yn/Y)]

Undertone [dM]= Mc-My

Experimental Procedure

In this study a commercial LDPE black concentrate was used to explore if the maximum jetness of carbon black could be manipulated by the addition of secondary color pigments. The concentrate was 40% carbon black, so it had to be let down to 10% to make is more workable and to ensure the weigh up measurements were accurate. A C.W. Brabender Prep-Mill Two Roll Mill was used for dispersion and was set to 132ºC (actual 135ºC/275ºF). It was calculated that 25g of the 40% concentrate would need to be mixed with 75g of low-density polyethylene (LDPE) in-order to obtain a 10% sample. The gap of the Two Roll Mill was checked and adjusted to 0.02′ with a feeler gauge. This was done before each dispersion. The LDPE was poured onto the rolls and the machine was turned on to 20 rpm. Some time was given to allow the resin to melt onto the rolls. The weighed-up concentrate was slowly added to the molten LDPE and the speed of the rolls was increased to 30 rpm. The LDPE dispersion was removed and placed back onto the rolls every 30 seconds,12 times using a brass scraper. After the last turn, the LDPE sheet was stripped from the mill and placed onto a Teflon sheet. The 10% masterbatch was then further let down using the same process as previous on the Two Roll Mill to increasing intervals of 0.1% up to 1%.

In-order to obtain a plaque of each sample for further examination, a strip of each masstone was pressed on the Platen Press. The Press was turned on and the dial set to 170ºC/338ºF. A piece of the masstone sample was placed between two Ferrotype plates with two Teflon sheets between them. The sample was pressed at 5,000 psi for 5 seconds and then removed to slowly cool at room temperature. At this point we were looking to determine the optimum loading of carbon black required to achieve the maximum jetness. A Multiangle X-rite MA9X Spectrophotometer was used to determine the jetness, blackness and undertone of the black masstone samples. When connected to the X-Color QC computer system, each plaque was measured at every concentration producing a table of data including L*a*b* and tristimulus values. This data was then collected and organized onto an Excel spreadsheet and plotted onto several graphs. At this point it was determined that the optimal concentration for carbon black is 0.7%. This was our starting point for the manipulation of jetness for the carbon black sample when introducing each secondary color pigment.

To investigate if the addition of color has an impact on the jetness, both carbon black and each of the color pigments were mixed during the dispersion process on the Two Roll Mill. Just as outlined in the steps above, a 10% masterbatch of carbon black and 10% masterbatch of each color was used for the weigh ups and mixed on the Two Roll Mill. Due to the determined optimum loading, 7g of the 10% carbon black sample was used for each dispersion while the secondary colors were added in 0.2%, 0.4%, 0.6%, 0.8% and 1.0% concentrations. This entire process was repeated several times for the addition of each color pigment. The colors mixed with carbon black for examination were Pigment Blue 60 (Indanthrone Blue), Pigment Blue 15:3 (Phthalocyanine Blue), Pigment Green 7 (Phthalocyanine Green), Pigment Red 179 (Perylene Maroon) and Pigment Violet 29 (Carbazole Violet).

As a secondary measure to visually see how the addition of the colour pigment affects the hue of carbon black, 1:10 tints were also made using the Two Roll Mill. Again 10% masterbatches of both carbon black and each sample were used for the weigh ups as followed: 94g LDPE, 4g TiO_2 and 2g of Masterbatch (1:10 ratio of black and color mixture). Once completed, each masstone sample was again pressed on the Platen Press and examined using the Multiangle X-rite spectrophotometer to obtain jetness, blackness and undertone data.

Data and Results

The L*a*b* and Tristimulus values obtained from the Multiangle Spectrophotometer were organized for each sample as shown in the table below:

Black Concentrate							
PBk.7 (g)	**X**	**Y**	**Z**	**DE***	**Blackness [My]**	**Jetness [Mc]**	**Undertone [dM]**
0.100	1.00	1.05	1.13	NA	**197.881**	**197.813**	**-0.068**
0.200	0.92	0.96	1.05	0.70	**201.773**	**202.137**	**0.364**
0.300	0.97	1.01	1.10	0.27	**199.568**	**199.654**	**0.086**
0.400	0.91	0.95	1.02	0.78	**202.228**	**201.808**	**-0.420**
0.500	0.95	0.99	1.06	0.46	**200.436**	**199.819**	**-0.617**
0.600	0.88	0.93	1.01	1.02	**203.152**	**203.760**	**0.608**
0.700	0.84	0.88	0.94	1.39	**205.552**	**205.061**	**-0.491**
0.800	0.85	0.90	0.97	1.27	**204.576**	**204.935**	**0.360**
0.900	0.90	0.94	1.02	0.86	**202.687**	**202.747**	**0.060**
1.000	0.90	0.94	1.03	0.90	**202.687**	**203.171**	**0.484**

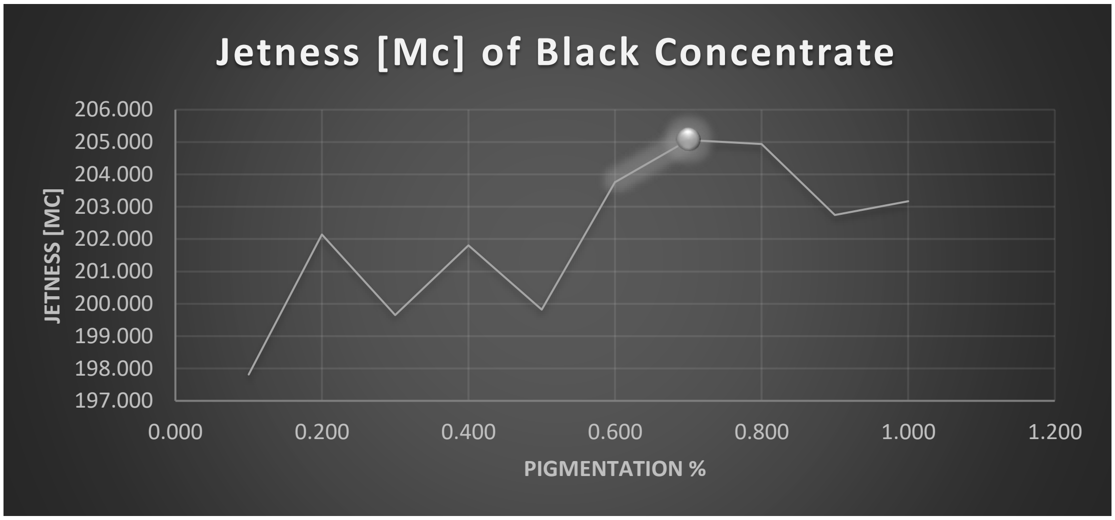

Figure 1. Jetness of the commercial carbon black concentrate, varying in pigment loading

According to the data collected with the spectrophotometer, as shown in Figure 1, the point in the graph with the highest jetness was 0.7% pigmentation. Once the optimal concentration of 0.7% was determined, the addition of secondary pigments began. After each dispersion, data was once again collected for each sample using the spectrophotometer and organized into tables and graphs such as below:

Black Concentrate w/ Pigment Blue 60								
PBk.7 (g)	**PB.60 (g)**	**X**	**Y**	**Z**	**DE***	**Blackness [My]**	**Jetness [Mc]**	**Undertone [dM]**
0.700	0.000	0.96	1.01	1.09	NA	**199.568**	**199.708**	**0.140**
0.700	0.200	0.89	0.90	0.98	1.69	**204.576**	**203.384**	**-1.192**
0.700	0.400	0.92	0.91	1.01	2.45	**204.096**	**202.773**	**-1.322**
0.700	0.600	1.00	0.97	1.13	3.00	**201.323**	**201.255**	**-0.068**
0.700	0.800	1.06	1.02	1.19	3.50	**199.140**	**198.788**	**-0.352**
0.700	1.000	1.00	0.94	1.10	4.25	**202.687**	**201.451**	**-1.236**

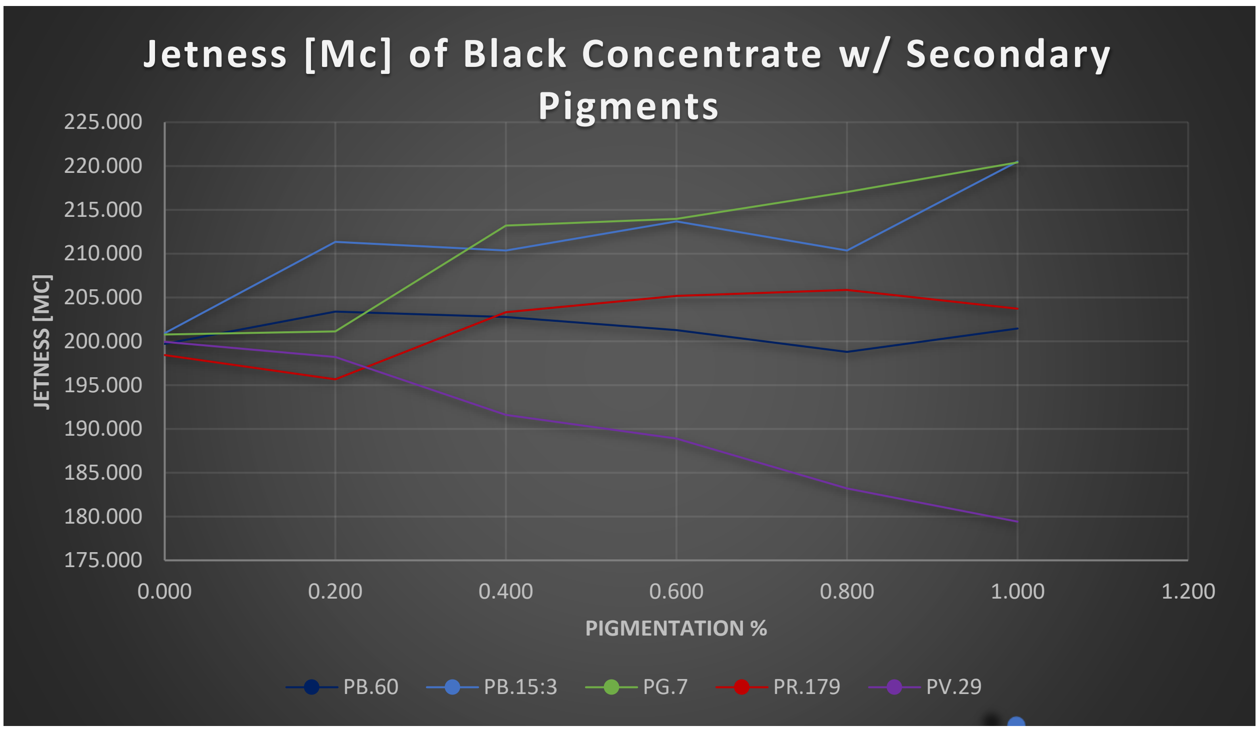

Figure 2. Comparison graph of Jetness of the commercial provided carbon black concentrate with each secondary color.

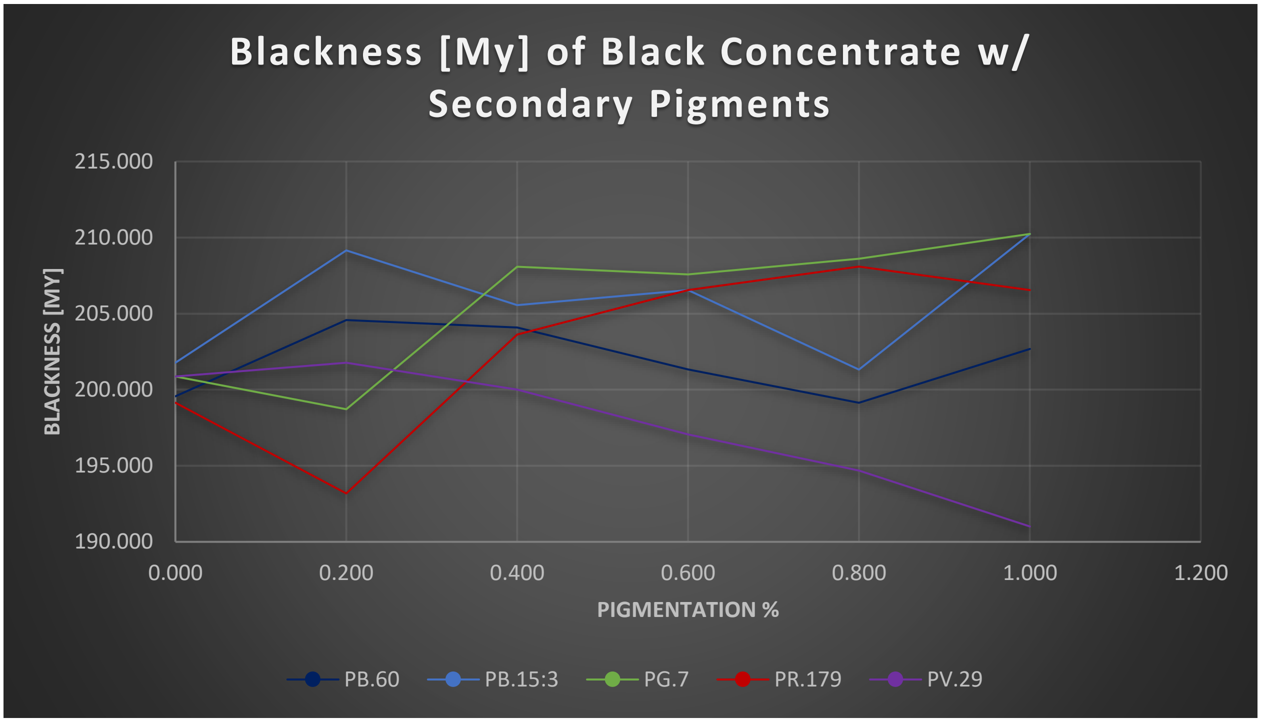

Figure 3. Comparison graph of Blackness of the commercial carbon black concentrate with each secondary color.

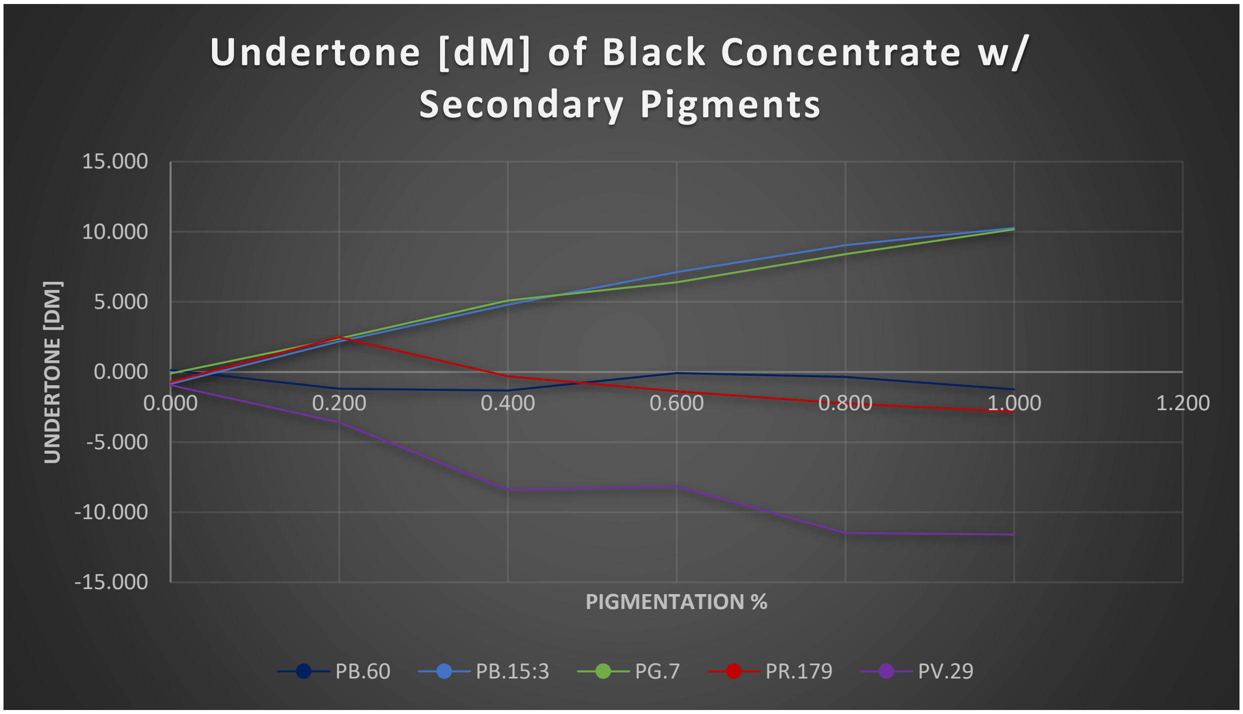

Figure 4. Comparison graph of Undertone of the commercial carbon black concentrate with each secondary color.

Interpretation of Data and Results

The addition of secondary pigments had different effects on the jetness, blackness and undertone of carbon black. Based on Figure 2, jetness was positively manipulated the most by the addition of PG.7 and PB.15:3. After the addition of these colors the initial maximum jetness increased significantly. PB.60 also had an immediate effect on the increase in jetness at the lowest pigmentation level although as it increased it began to level off. The only color to have an obvious negative effect on the jetness was PV. 29. The addition of this color immediately impacted the black causing it to weaken as higher concentrations were added allowing the development of a visually brown tone. This data directly correlates with Figure 4, where the undertone data looks fairly similar to that of jetness. With the increase of pigment, the addition of PG.7 and PB.15:3 produced a bluer shade black compared to PV. 29 that produced a redder shade black. The addition of PR.179 did not influence either jetness or undertone compared to the other colored pigments used. While PB. 60 also did not have much effect on the undertone thus keeping a neutral black shade.

Blackness is where the most variation is seen. In Figure 3, as the concentration of secondary pigment is increased, PB.15:3, PG.7, and PR.179 produced visually blacker plaques than the other two pigments used. PB. 60 did produce visually blacker plaques at the lowest pigmentation levels, but it began to weaken as pigmentation increased. This was verified when evaluating the 1:10 tints made for each additional color mixture. As the concentrations of each were increased, the hue of the tints changed significantly for most colors. For PR.179, the tints look quite similar with not much change in hue, while PB.60, PB.15:3 and PG.7 had a very blue/green hue and PV.29 had a very red/purple hue.

Conclusion

In conclusion, colored pigments can be used to improve the jetness, blackness and undertone in a formulation. PB.60 and PB.15:3 showed immediate impact at the 0.2% pigmentation level for increasing jetness and blackness while PB.60 had very little effect on undertone. This would allow for the best economic impact when using secondary pigments since very little is needed to get the desired effect. Although the addition of PG.7 improved jetness, blackness and undertone, higher pigment loading is needed to achieve this, thus making it not as economically friendly. Overall, this leads us to believe that blue pigments are best to use in terms of the financial benefit to achieve the desired product. The addition of this colored pigment allows the manufacturer to achieve the desired quality of black without having to use such a big quantity of carbon black itself. This can have the potential of not only cutting costs in producing end products that contain carbon black as it is quite an expensive pigment, but also reducing the amount of mess created from a manufacturing standpoint. A financial benefit could incur for many industries, especially in automotive and electronics.

PR.179 had very little visual effect and did not produce much improvement or benefit to the jetness, blackness and undertone of the carbon black. In addition, PV.29 decreased all three characteristics of the carbon black and produced a brown tone. Although this is not beneficial to increase jetness, it could be of benefit when needing to tone something redder in color. All in all, warm colors have a detrimental effect along with no improvement for the shade of black.

Acknowledgments

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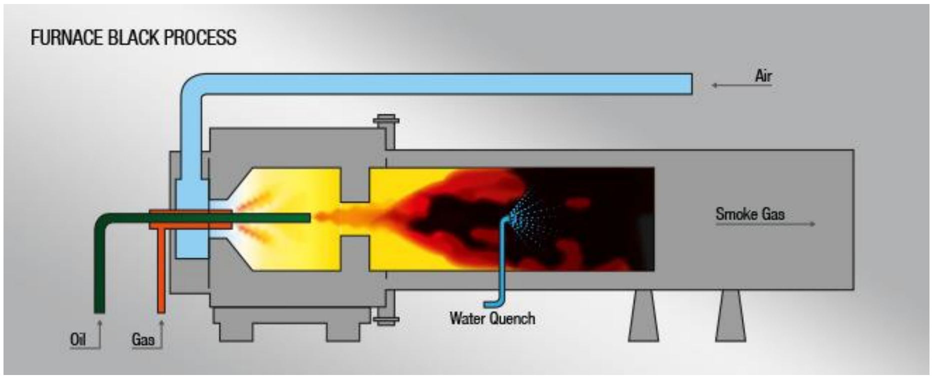
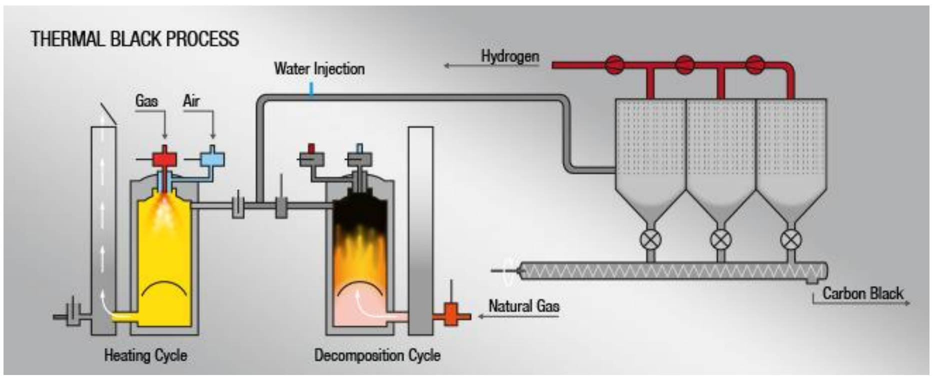
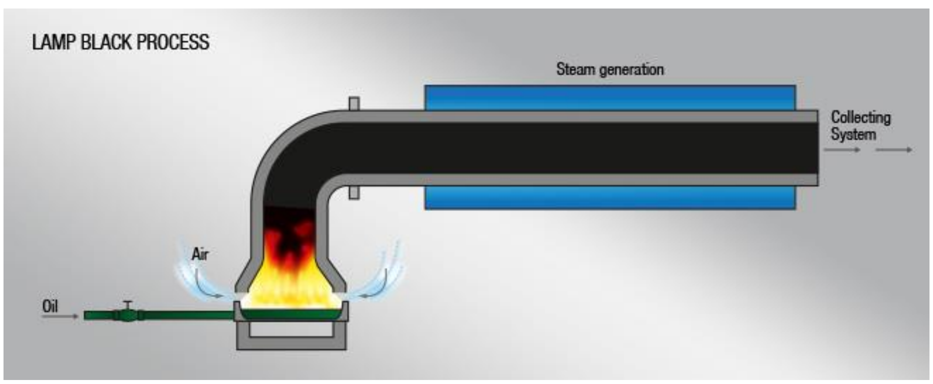
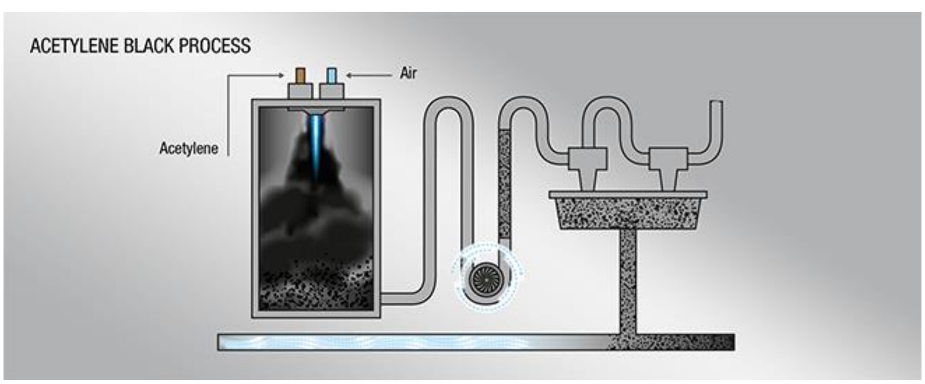
Illustrations









Illustrations cont'd

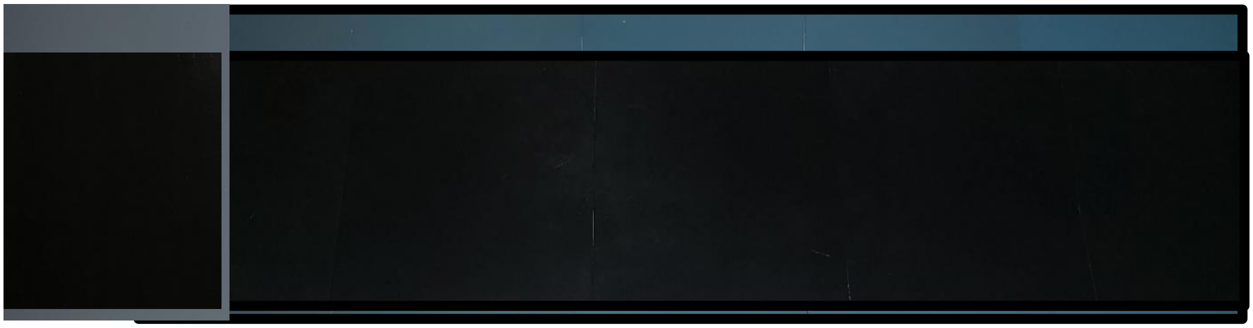
Pigment Plaques

Black Concentrate   Pigment Blue 60 (Indanthrone blue) Masstone

1:10 Tint   Pigment Blue 60 (Indanthrone blue) 1:10 Tint

Black Concentrate   Pigment Blue 15:3 (Phthalocyanine blue) Masstone

1:10 Tint Pigment Blue 15:3 (Phthalocyanine blue) 1:10 Tint



Black Concentrate Pigment Green 7 (Phthalocyanine green) Masstone

1:10 Tint Pigment Green 7 (Phthalocyanine green) 1:10 Tint

Black Concentrate Pigment Red 179 (Perylene Maroon) Masstone

1:10 Tint Pigment Red 179 (Perylene Maroon) 1:10 Tint

Black Concentrate Pigment Violet 29 (Carbazole Violet) Masstone

1:10 Tint Pigment Violet 29 (Carbazole Violet) 1:10 Tint