

RESEARCH PROGRESS IN LASER MARKING TECHNOLOGY FOR ELECTRICAL PRODUCTS

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Abstract: This article introduces the laser marking mechanism and commonly used laser marking machines. Based on the survey of the domestic electrical industry, it focuses on the commonly used laser marking machines. Label plastics and the current status of technology; introduce the characterization method of laser marking effect, and characterize the laser marking effect of different materials in examples, and at the same time It also briefly introduces the debugging of laser marking process parameters; finally, it summarizes the technical bottlenecks of commonly used laser marking plastics and looks forward to the development direction of domestic laser marking materials and technology.

Keywords: Electrical; Laser marking; Plastic; Characterization method

1 Introduction

Electrical products need to be marked before leaving the factory. Its surface reflects specific product information: such as company name and trademark. Technical parameters, barcodes and production information, etc. traditional surface printing Although brush technology can meet the above functional requirements, the emerging laser Marking technology is increasingly being used in low-voltage electrical products logo. This is because compared to traditional printing technology, laser marking. It has the following advantages: (1) It is more convenient and efficient, with fast marking speed and relatively few processes; (2) It is more suitable for short-cycle information marking, such as production Production date and code, etc.; (3) More environmentally friendly, because no ink harmful to the human body is required; (4) The logo formed by laser marking is relatively more wear-resistant. This article will combine the application requirements of laser marking in the electrical industry, focusing on Introduce the technical status of commonly used laser marking materials in China, and use a Some commonly used laser marking materials are taken as examples to introduce the quantitative characterization of laser marking. Method, and briefly introduce the laser marking process and debugging.

1.1 Laser Marking Machine Mechanism

At present, laser marking effects can basically be divided into two categories: one The class is based on dark-colored materials marking light-colored effects. This article is referred to as It is "black and white"; one type is based on light-colored materials to mark dark colors. The effect is referred to in this article as "white versus black".

When the laser beam acts on the plastic, the light energy is converted into heat energy, and the material After the material surface absorbs energy, it will melt, foam, change color, and vaporize. Or carbonized, thereby forming graphic and text marks that are different from the background. [2]. To achieve this, the plastic must absorb the corresponding wavelengths of light, If the plastic cannot absorb the laser of the corresponding wavelength well, it will not be able to produce a good marking effect. When laser marking, for "white For "black and white" materials, the plastic will mainly undergo carbonization and produce dark marks; for "black and white" materials, the plastic will mainly undergo gasification and swelling. bubbles, resulting in light-colored marks. A type of material that cannot be laser printed The extreme case is that the material does not absorb light, and the laser passes directly through the plastic without Any mark will be generated. The schematic diagram of laser marking mechanism is shown in Figure 1.

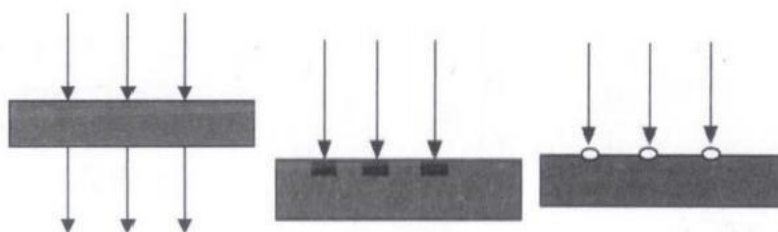


Fig. 1 Schematic diagram of laser marking mechanism

In many cases, in order to obtain good laser marking effects, Laser marking additives need to be added to the material. Laser marking additives The function is to change color directly under the action of laser to produce marks, or to enhance Absorption of laser light by plastics.

1.2 Laser Marking Machine Classification

Depending on the laser light source, Generally, it can be divided into 4 types of laser marking machines 3- sI. (1) Continuous wave carbon dioxide (CO₂) laser, which produces The laser wavelength is 10640 nm ; (2) Neodymium -doped iridium neodymium laser (Nd : YAG Laser), this type of laser can produce laser light of different wavelengths, But the common one is 1064 nm Laser; (3) Excimer laser, This type of laser mainly produces laser light in the ultraviolet spectrum band (this type of laser Optical marking machine is commonly known as UV laser marking machine); (4) Laser diode Pump (DPSS) Lasers and fiber lasers. In practical application, the production Raw 1064 nm Laser Nd:YAG Laser marking machines are widely used in China. The laser marking discussed in this article, if nothing special is said clear, indicating that Nd:YAG is used to generate 1064 nm laser. laser marking machine.

2 Laser Marking Materials

Commonly used laser marking materials and performance requirements in the low-voltage electrical industry Find: (1) Laser marking materials mainly include polycarbonate materials (PC), polyamide resin material (PA), polybutylene terephthalate Ester material (PBT) or polyethylene terephthalate material (PET);(2) These materials are generally glass fiber reinforced composites materials; (3) Based on the application requirements of low-voltage electrical insulation materials, these Materials are generally required to have certain flame retardancy (abnormal heat resistance) and surface properties. Surface insulation properties; (4) These materials themselves generally have appearance colors color requirements. Compared to materials that do not require laser printing, laser marking materials It is generally necessary to add some laser marking additives to improve laser marking Effect. For this purpose, these materials are often used within the low-voltage electrical industry When adding laser marking, the material properties after laser marking can be compared with those before adding Performance comparison, evaluate laser marking material color, insulation, flame retardant and even Whether the strength meets the application requirements.

According to the author's material application experience, commonly used in the low-voltage electrical industry The marking effects of laser-markable glass fiber reinforced flame retardant materials are summarized in Table 1 shown.

Table 1 Marking effects of commonly used laser markable materials

matrix resin	" white beat black "	" black beat white "
PC	Marking is easy and the effect is good	Difficult to mark, color is yellowish
PA	Difficult to mark, color is too light	Marking is easy and the effect is good
PBT	Difficult to mark, color is too light	Difficult to mark, color is yellowish

Combined with the difficulty of marking, the following mainly analyzes and discusses PC "Black on white", PA66 "white on black", PBT "white on black" materials and laser Current research and application status of optical printing technology.

2.1 Polycarbonate Material (PC)

PC is often used as a mask for frame circuit breakers. This type of mask is The surface can reflect some product technical parameters, two-dimensional Code etc. Generally, this type of mask is mainly dark-colored, and its laser marking is In the category of "black versus white". At present, PC is "black and white", mainly in color. The root cause of the problem of yellowish color and low contrast lies in the PC in high It is easy to form char at high temperatures and is more suitable for "white versus black" applications. although In this way, due to the needs of practical applications, there are still many studies and reports on the "black versus white" aspect of PCs.

General Electric Company once developed a "black chip" suitable for electrical switches. "White" light-colored laser marking composition. Its main features are : Copper alkylate with a spinel structure is added to the polycarbonate matrix. and up to 0.05% (mass fraction, the same below) of carbon black. Acrylic acid The average

particle size of copper is 0.35~5.5 μ m, and the preferred addition amount is 0.7%~ 1%. Polycarbonate foamed in laser-irradiated area to show on dark background Forms light colored markings; the copper alkylate spinel is well separated within the matrix Blur enhances the contrast of bright colors on a dark background. This method forms a bright mark on a dark background with high contrast without changing the background color. distortion.

Kingfa Company uses black high-gloss PC as the basic formula system. PC "black against white" research. Research shows that: (1) carbon black is more suitable It matches the color matching of "black and white" PC. This may be because carbon black has a certain effect on light. It has a certain absorption effect and can better assist foaming; graphite also has the ability to absorb The ability to absorb energy, but the coloring power itself is not enough, and it will affect the high The effect of light; (2) Certain fillers (such as metal oxides) The formula system can play a supporting role in the marking effect and should be based on different Detailed screening of the same formula system; (3) Despite the contrast of laser marking It has been improved to a certain extent, but there are still problems with reddish and yellowish colors. In addition, Kingfa also announced a halogen-free flame-retardant polycarbonate compound P that can be laser marked. The compound mainly adds a silicone copolymerized PC and a type of silane coupling agent, and passes through carbon black Make dark colors. The reference dosage of silicone copolymerized PC is 20%; silane coupling The key feature of the coupling agent is that it contains a benzene ring and a silicon-oxygen bond, preferably two The preferred dosage of phenylcarboxysiloxane is 1% to 10%. silicone The main function of copolymerized PC and silane coupling agent is to strengthen the foam Structural strength. Taking into account the thin-wall characteristics, appearance and Strength requirements, weight average molecular weight of polycarbonate (M) Preferably 15,000~80,000. The flame retardant of this compound uses sulfonate, Dosage <20%. The polycarbonate composite is a halogen-free flame retardant material. It has high gloss and V-0 flame retardant level, and can be suitable for "black and white", mainly Used in electrical products.

Wuxing Technology Co., Ltd. also announced a similar laser Marked polycarbonate composite country. The composite uses laser The standard additive is mainly acetic acid copolymer, and the compound contains silicone copolymer. PolyPC. The compound also uses carbon black to create darker colors and methylpropyl Methyl acrylate-butadiene-styrene (MBS) terpolymer as Compatibilizer and added phosphate flame retardant. The compound produced It not only has good laser marking performance, but also has halogen-free flame retardant, Excellent appearance gloss, good mechanical properties and surface insulation properties, Therefore, it can be used for laser marking of appearance parts of electrical products.

2.2 Polyamide Resin Material

Polyamide resin, especially PA66 or PA6, is often used in Housings for electronic and electrical components. However, polyamide itself is difficult to be carbonized ization, "white to black" seems more difficult, but adding appropriate laser printing Marking additives can achieve good laser marking effects.

Mitsubishi Engineering Plastics has invented a series of laser marking Excellent polyamide resin composition°. This composition is particularly suitable for "White against black", the difference in brightness before and after the mark ΔL reaches more than 40, and the mark clear memory; in addition, the composition also fully maintains good mechanical Mechanical impact strength, flame retardant properties and insulation properties. Example of laser printing The main components of standard additives are traditional flame retardants: halogen-containing compounds and antimony trioxide. These two substances can be used alone, or Can be used together. Analyzing from examples, they are both halogen compounds. The effect of polydibromophenylene ether as a laser marking additive is slightly better than that of bromination Polystyrene; when antimony trioxide is used as a laser marking additive, the material appears white with particularly high brightness. For color mixing needs, the material can Add white pigment titanium dioxide; to increase strength, glass can be added Glass fiber; elasticity can be added to improve toughness and impact resistance body. Add these substances, adjust the formula and debug the marking process technology, you can get good laser marking effects.

Dang Xiaorong¹ also invented a polyamide group that can be laser marked compound. The composition uses polyhedral oligomeric silsesquioxane as the Color auxiliary, the composition composition is roughly: 100 weight fraction of polyamide, Polyhedral oligomeric silsesquioxane 0.01~15 weight fraction. Pass the test Comparison of experimental data found that after adding polyhedral oligomeric silsesquioxane, the The blackness is increased by 100%~200%, and the impact strength and toughness are improved. to significantly improve. The composition can be used outside the electronic and electrical industry Laser marking of shells. It is worth noting that the laser marking material The flame retardant system is a halogen-free flame retardant system, so it is more environmentally friendly and has an insulated surface. The edge performance is more superior.

Wang Xiaolan and others used two laser marking systems, both of which Get good laser marking effect." One is to add a table to PA6 Mica and acrylic powder rubber covered with SnO₂. research and development Now: When the mass fraction of mica is 1% and the mass of acrylate powder rubber When the score is 1%, PA6 laser marking has the best effect. The other is in Added product name LS285 to PA 6 laser marking additives, and Combined with

acrylic powder rubber and titanium dioxide. Research shows that when the mass fraction of LS285 reaches 0.5%, PA6 can achieve good laser marking. The effect is that the marked font lines are smooth and the marks are clear; the quality score is 0.5% titanium dioxide can significantly improve PA6 Contrast of laser marking, This is because TiO_2 decomposes under the action of laser to produce black TiO ; and the acrylate powder rubber with a mass fraction of 2% is not only Promote the material's absorption of laser and also improve PA6 impact toughness.

2.3 Polybutylene terephthalate (PBT) material

Laser marking of polybutylene terephthalate materials is also widely used in electrical products, such as contactor coil bobbins and a casings of some products. Polybutylene terephthalate "white and black" The main problem is that the printed fonts are light and yellowish. This is mainly because Because PBT has poor absorption of 1064 nm laser.

Liu Chunlin and others from Changzhou University used Sb_2O_3 as laser marking Additive, PBT/ Sb_2O_3 with excellent performance is prepared through melt blending method composite materials, and their laser marking mechanism was analyzed. Research shows that when the Sb_2O_3 mass fraction reaches 3%, the PBT/ Sb_2O_3 complex The composite material has good laser marking characteristics, and the front and rear of the laser marking are clearly visible. The absolute value of dark contrast AL is close to 37; Sb_2O_3 energy absorption in composite materials Collect the heat generated by the laser and carbonize and pyrolyze the surrounding PBT into amorphous form carbon substances without any change in chemical structure; due to After marking, the degree of carbonization of the composite material deepens, and the composite material is marked The color deepens; in addition, during the marking process, PBT A small amount of carbon and Oxygen reacts to form carbon dioxide gas and escapes, causing the laser marking area The oxygen content in the domain increases.

In a 2009 patent, Kingfa Technology disclosed a Glass fiber reinforced polyterephthalate with laser printing marking capabilities Butanediol ester resin composition I³, This composition mainly uses imperial DSM The company produces a product called Micabs A206 Laser marking additives. With a suitable formulation system, the composition It can meet the functional requirements of "white on black" or "black on white" and has good mechanical properties.

In another patent, Kingfa Technology also disclosed a halogen-free flame-retardant polyester with laser marking function and its preparation method. Should The laser marking agent in the composition is preferably copper phosphate hydroxide, with a mass of The fraction is within the range of 0.5%~5%; halogen-free flame retardant is selected from +3-valent organic Phosphate and melamine polyphosphate flame retardant compound, mass fraction The number is within 10%~30%. Glass fiber reinforced by this method In addition to maintaining good In addition to good laser marking effect, it also has good insulation properties and mechanical properties. Performance, the composition has a comparative tracking index (CTI) of 600V, The flame retardant grade reaches V-0 level, which is fully suitable for flame retardant and low-voltage electrical industry. Environmental requirements. However, it is worth noting that PBT is not mentioned in the patent. Application of "white against black". At present, domestic flame-retardant PBT is "in vain" "black", especially halogen-free flame retardant PBT "white black" material is still a Technical weaknesses.

3 CHARACTERIZATION OF LASER MARKING EFFECT

At present, the commonly used characterization method of laser marking effect is qualitative characterization, that is, laser marking is performed directly on the material, and the marked material is directly used for comparison and reference of laser marking effect. However, This non-quantified characterization reduces the accuracy of the characterization and is inconvenient for the parameterized expression of the laser marking effect; while the quantitative characterization of the laser marking effect is helpful for the accurate expression and quality control of the laser marking effect of the material. According to the testing method, the common quantitative characterization method of laser marking effect is mainly the colorimeter method.

The colorimeter method mainly adopts the International Standard Illuminating Institute (CIE) Established CIE Lab color space I⁹. CIE Lab color space is represented by L value represents color brightness, a represents color red and green value, b represents color yellow blue value. Combined with the author's actual testing experience, first test the unlaser printed Color parameters of the marked area, expressed as L_0 , a_0 , b_0 , and then test the laser The color parameters of the marking area are expressed as L_1 , a_1 , and b_1 . Calculate $\Delta L=L_1-L_0$ respectively, $\Delta a=a_1-a_0$, $\Delta b=b_1-b_0$, ΔL is positive, which means whiter, AL Negative means darker; Δa is positive, means redder, Δa Negative means partial Green; if Δb is positive, it means more yellow, and if Δb is negative, it means more blue. Color contrast $\Delta E=(\Delta L^2+\Delta a^2+\Delta b^2)^{1/2}$. These four parameters AL, Aa, Δb , AE Accurately describes laser marking color effects, however sometimes to simplify Description can only use some parameters, but AL is essential.

Table 2 shows 6 types of electrical appliances selected based on the author's actual experience. Flame-retardant laser marking materials for gas product applications, among which numbers 1 to 5 are Halogen-free flame

retardant materials, No. 6 are ordinary brominated flame retardant materials. first The model used is YAG-T120C Infrared laser marking machine for marking mark, the mark pattern is 20 mm in diameter circular area; then use The model is Data color DC 650 colorimeter for color measurement Test, the test results are summarized in Table 3.

Table 2 Laser marking material information

serial number	Brand name	factory	material ingredient	color	Flame retardant system	retardant
	PA66-NPG25 A7A-G0121	blond	PA66GF25 FR	light gray	Halogen-free	flame retardant
2	PA66-NPG25 A3A-G0035	blond	PA66GF25 FR	dark gray	Halogen-free	flame retardant
3	JH720-R0G10D C7A-G0237	blond	PCGF10 FR	light gray	Halogen-free	flame retardant
4	JH720-R0G10D C3A-G0095	blond	PCGF10 FR	dark gray	Halogen-free	flame retardant
5	PBT-NPG30 LMB8A-G0068	blond	PBTGF30 FR	light gray	Halogen-free	flame retardant
6	PBT3730FG KI902960	Kumho	PBTGF30 FR	light gray	Bromine	flame retardant
7	Makrolon M.6485C 15C109MA	bayer	PCGF10 FR	dark gray	Halogen-free	flame retardant

Table 3 Laser marking effect data comparison

serial number	L _o	do	b _o	L _i	a _i	b _i	ΔL	ΔE	Marking effect
	74.81	-0.18	1.16	47.69	-0.83	3.19	-27.12	27.20	Dark gray, slightly lighter
2	35.61	-0.07	-0.36	65.83	0.54	6.66	30.22	31.03	light gray, fine
3	76.41	0.11	1.15	38.09	0.36	0.04	-38.32	38.34	dark gray, fine
4	33.68	-0.33	0.55	66.12	0.47	14.48	32.44	35.31	Light gray, slightly yellowish
5	74.99	-0.02	0.49	62.99	0.39	2.66	-12.00	12.20	Dark gray, lighter
6	75.43	0.04	1.45	37.62	0.43	0.85	-37.81	37.82	dark gray, fine
7	35.52	-0.45	0.13	62.41	0.65	1.26	26.89	26.94	light gray, fine

JH 720 - ROG 10D C 3A-G0095 glass fiber reinforced polycarbonate Material laser marking is "black and white", but there is still a problem of yellowing; the brand No. Makrolon M.6485C 15C109MA glass fiber reinforced polyethylene Carbonate material laser marking PC "black and white" effect is good; no halogen resistance The "white against black" effect of burning PBT is not good, bromine-based flame retardant PBT is more suitable PBT laser marking.

4 LASER MARKING PROCESS

In order to obtain stable and high-quality laser marking effects, in addition to In addition to materials, the adjustment and control of the laser marking process cannot be ignored. See. Process parameters of laser marking effect, including laser marking machine Focal length, marking times, marking power, heat release time, current intensity degree, frequency and step size etc. 1°. In practical applications, the focal length is selected Finally, the most obvious impact on the laser marking effect of plastic products is Operating current, switching modulation frequency and step size.

After obtaining the optimal process parameters for a specific formula material, This set of process parameters can be controlled to obtain stable and good laser marking effects.

5 CONCLUSION

At present, the pace of upgrading of electrical products is accelerating, based on environmental protection Demand and efficient and flexible operation methods, more and more electrical manufacturers will consider choosing laser marking to replace traditional printing technology. However, the technical bottlenecks of some laser marking materials will restrict this process. For example, most domestic material manufacturers have not yet been able to solve the problem of yellowing of flame-retardant PC, the problem of "black on white", the problem

of "white on black " of halogen-free flame-retardant PBT, and the light "white on black" of halogen-free flame-retardant nylon. The problem. Although some domestic material manufacturers are able to make laser marking materials and even apply for patents, high-quality products as the core of the technology High-quality laser marking masterbatch or laser marking powder mostly relies on some foreign countries. Well-known manufacturer. In the future, as the demand for laser marking market increases, With the rapid development, it is expected that relevant domestic manufacturers can also break the foreign monopoly and produce laser agents and masterbatch that meet various laser marking needs.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

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